Stability of heteroazulene-substituted tropylium ions: synthesis and properties of the (2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)tropylium ion, and its oxygen and nitrogen analogues

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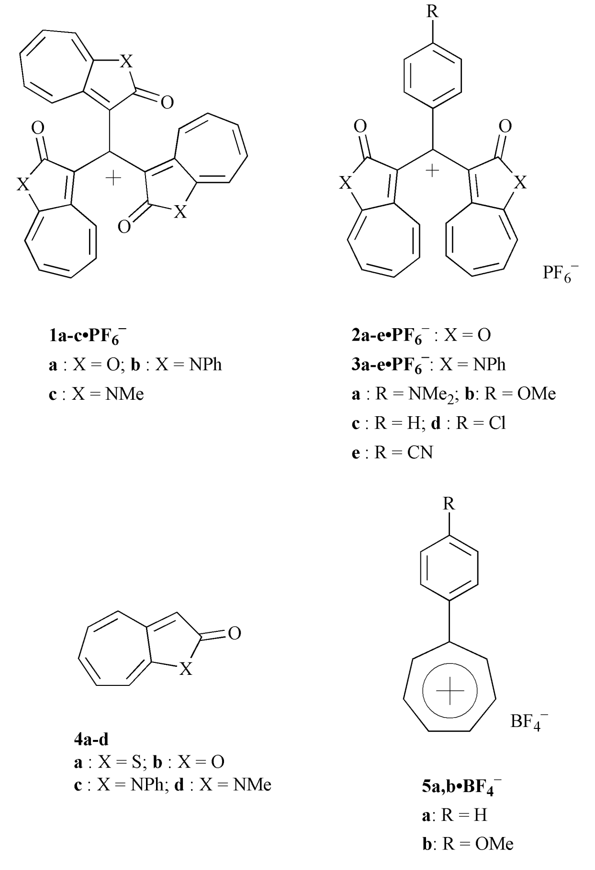
Synthesis and properties of a novel type of heteroazulene-substituted tropylium tetrafluoroborate, 2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yltropylium tetrafluoroborate, and its oxygen and nitrogen analogues, **9a–d·BF$_4^-$** are reported. The synthesis is based on a simple reaction of the tropylium ion with the corresponding heteroazulenes in the presence of NEt_3, followed by oxidative hydrogen abstraction with DDQ and subsequent exchange of the counter-anion by using aq. HBF_4 solution. The stability of the tropylium ion derivatives **9a–d** is found to be in the order **9a** < **9b** < **9c** < **9d** from pK_{R+} values of 3.2–5.7 obtained spectrophotometrically and reduction potentials measured by cyclic voltammetry (CV). The important canonical structures for the cations **9a–d** are discussed on the basis of the ^{1}H and ^{13}C NMR spectral data and the energy levels of HOMOs of heteroazulenes as well as the stable conformation obtained by AM1 method (MOPAC97). A good linear correlation between the pK_{R+} values and the reduction potentials was obtained for cations **9a–d**. The stabilizing effect of heteroazulenes toward cations **9a–d** is similar to that of heteroazulene-substituted methyl cations based on the similarity of the regression line slopes.

Introduction

We have recently reported the synthesis and properties of tris(heteroazulen-3-yl)methyl cations **1a–c**[1] and two series of bis(heteroazulen-3-yl)(4-substituted-phenyl)methyl cations **2a–e** and **3a–e**.[2] The pK_{R+} values of **1a–c** (pK_{R+} = 9.7–13.1), **2a–e** (pK_{R+} = 12.4–7.9), and **3a–e** (pK_{R+} = 13.9–11.1) are remarkably higher than that of the triphenylmethyl cation (pK_{R+} = −6.44).[3] This feature shows that heteroazulenes such as 2*H*-cyclohepta[*b*]furan-2-one **4b**,[4] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **4c**,[5] and 1,2-dihydo-*N*-methylcyclohepta[*b*]pyrrol-2-one **4d**[6] (Fig. 1) have large stabilizing effects toward methyl cations. The stabilizing effect can be ascribed to the electronic effect expressed by π-electron donation and the steric effect of the bulky heteroazulene units.[1] The reaction of **1**, **2** and **3** with the hydroxide ion becomes unfavorable due to strain destabilization of the corresponding methanol when the central carbon is forced into sp^3 hybridization. An independent evaluation of these two stabilizing effects seems to be difficult. On the other hand, the synthesis and properties of many substituted tropylium and cyclopropenylium ions, *i.e.*, (4-substituted-phenyl)tropylium **5a,b**,[7] (thiophen-2-yl)tropylium,[8] (azulen-1-yl)tropylium ions,[9,10] tris(azulen-3-yl)cyclopropenylium ion,[11] and their derivatives, have been investigated extensively. In these cations, the positive charge delocalizes to the seven- or three-membered ring, and the steric hindrance of these cations toward the hydroxide ion is expected to be smaller than that of heteroazulene-substituted methyl cations **1a–c**, **2a–e** and **3a–e**. From this viewpoint, we studied the synthesis and properties of (2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)-, (2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-, (1,2-dihydro-2-oxo-*N*-phenylcyclohepta-[*b*]pyrrol-3-yl)-, and (1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)tropylium ions **9a–d**. The HOMO and LUMO of 2*H*-cyclohepta[*b*]thiophen-2-one **4a**[12] are suggested to be lower than those of **4b–d** based on MO calculations (*vide infra*). Thus, the evaluation of the stabilizing effect of **4a–d** toward cations **9a–d** seemed to be interesting. The reduction potentials and the pK_{R+} values of cations **9a–d** were measured to clarify the thermodynamic stability. On the basis of the NMR spectral studies, the important contribution of the canonical structures of cations **9a–d** is rationalized. We report herein the results in detail.



1a-c•PF$_6^-$
a : X = O; **b** : X = NPh
c : X = NMe

2a-e•PF$_6^-$: X = O
3a-e•PF$_6^-$: X = NPh
a : R = NMe$_2$; **b**: R = OMe
c : R = H; **d** : R = Cl
e : R = CN

4a-d
a : X = S; **b** : X = O
c : X = NPh; **d** : X = NMe

5a,b•BF$_4^-$
a: R = H
b: R = OMe

Fig. 1

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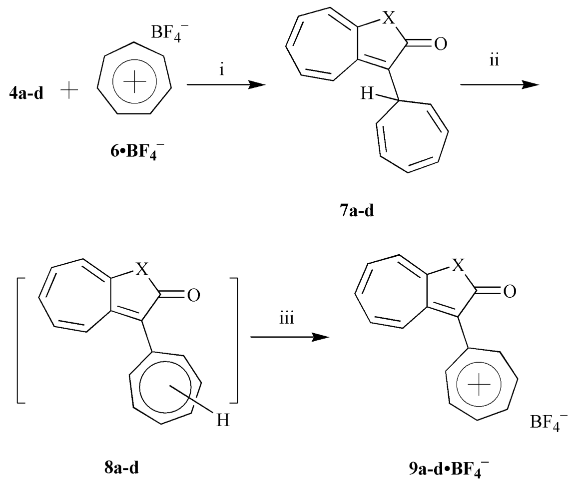
Table 1 Results for the preparation of tropylidene **7a–d** and tropylium salt **9a–d·BF$_4^-$**

Heteroazulene	Tropylation Product	 Yield (%)	Hydride abstraction Product	 Yield (%)
4a	**7a**	33	**9a·BF$_4^-$**	41
4b	**7b**	85	**9b·BF$_4^-$**	97
4c	**7c**	90	**9c·BF$_4^-$**	100
4d	**7d**	98	**9d·BF$_4^-$**	100

Results and discussion

The heteroazulenes **4a–d** reacted smoothly with tropylium tetrafluoroborate **6·BF$_4^-$** in CH_3CN at rt to give the tropylidene derivatives **7a–d** in modest to good yields, respectively (Scheme 1, Table 1). The low yield of **7a** as compared with those of **7b–d** is suggestive of the low nucleophilic property of **4a**. The compounds **7a–d** form orange or yellow crystals. The compound **7b** is known and has been identified on the basis of comparison of the physical data.[13] The structures of **7a,c,d** were assigned on the basis of the comparison of their IR, ^{1}H and ^{13}C NMR spectral data with those of **7b**, as well as the elemental analyses and mass spectral data. Thermal hydrogen migration of **7a–d** giving mixtures **8a–d** and subsequent treatment with DDQ followed by anion-exchange reaction with aq. 42% HBF_4 gave salts **9a–d·BF$_4^-$** in modest to good yields. The results are also summarized in Table 1.



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

Scheme 1 *Reagents and conditions*: i, NEt_3, CH_3CN, rt; ii, xylene, reflux, 1 h; iii, (a) DDQ, CH_2Cl_2, (b) 42% aq. HBF_4, Ac_2O.

The structures of **9a–d·BF$_4^-$** were assigned on the basis of their spectral data and elemental analyses. Mass spectra of the salts **9a–d·BF$_4^-$** ionized by FAB exhibited the correct $M^+ - BF_4$ ion peaks, which are indicative of the cationic structure of these compounds. The characteristic bands for the counter ion BF_4^- are observed at 1084–1058 cm^{-1} in the IR spectra of **9a–d·BF$_4^-$**, respectively. These features also support the cationic nature of the compounds. The UV–vis spectra of cations **9a–d** in acetonitrile are shown in Fig. 2. The spectra of **9a–d** are similar and the longest wavelength absorption maximum of **9b** shows a blue-shift of 18 nm and those of **9c,d** show a red-shift of 11 nm compared with that of **9a**. In the ^{1}H NMR spectra, all proton signals of **9a–d·BF$_4^-$** appear as sharp signals and the protons of the tropylium moiety have C_2 symmetry. Thus, the heteroazulene ring of **9a–d** can rotate freely in the NMR time scale. This feature is completely different from that of heteroazulene-substituted bulky methyl cations **1a–c**, **2a–e** and **3a–e**, in which the proton signals of the heteroazulene moieties are recorded as broad signals.[1,2] The ^{13}C NMR spectra of **9a–d·BF$_4^-$** are recorded and assigned by using the C–H COSY spectra. The average chemical shifts (δ_{av}) of the tropylium moieties of **9a–d** and **6** as well as the chemical shift-differences ($\Delta\delta_{av}$) between **9a–d** and **6** are summarized in Table 2. The average chemical shifts ($\Delta\delta_{av}$) of the protons and carbons in the ^{1}H and ^{13}C NMR spectra of **9a–d** are shifted to higher field as compared with those of **6** in the order **9a** < **9b** < **9c** < **9d**. This features implies that the positive charge is more delocalized to the heteroazulene-unit in the order **9a** < **9b** < **9c** < **9d**. A large π-conjugative effect is obtained with a more planar conformation, while the more planar conformation experiences steric hindrance between the heteroazulene and tropylium moiety. The most stable conformations of **9a–d** obtained by AM1 method (MOPAC97)[14] are summarized also in Table 2. The dihedral angle (θ) and the bond length express deviation from the plane of the heteroazulene from the plane of the tropylium moiety and the C–C bond distance between C3 and C1′ carbon atoms (Fig. 3). The bond length becomes longer in the order **9a** > **9b** > **9c** ≈ **9d**, and the dihedral angle (θ) in the order **9a** > **9b** > **9c** ≈ **9d**. Thus, the NMR data as well as the stable conformation obtained by the AM1 method show that the contribution of the canonical structures **B** and **C** becomes more important in the order **9a** < **9b** < **9c** < **9d** (Scheme 2).

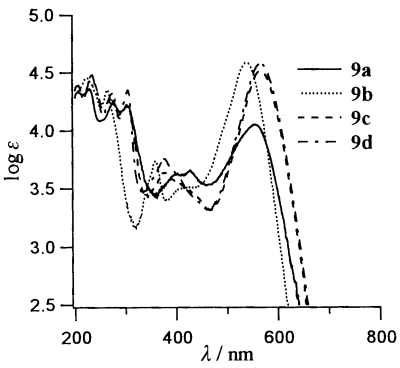
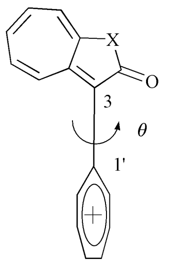
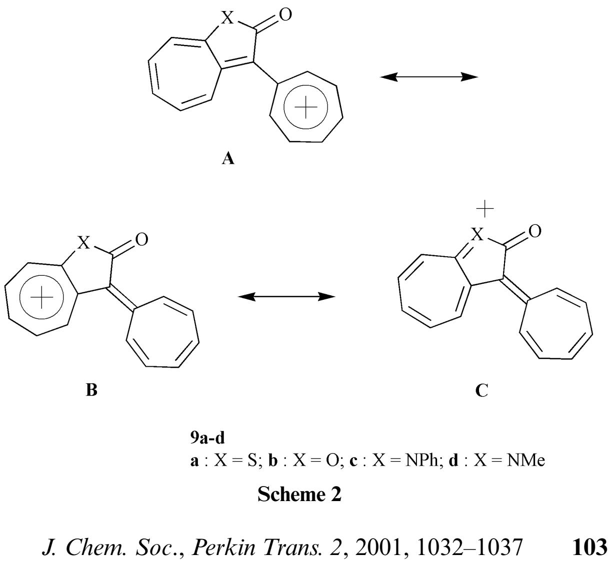


Fig. 2 UV–vis spectra of cations **9a–d** in acetonitrile.



9a-d
a : X = S
b : X = O
c : X = NPh
d : X = NMe

Fig. 3 Conformation of **9a–d**.



9a-d
a : X = S; **b** : X = O; **c** : X = NPh; **d** : X = NMe

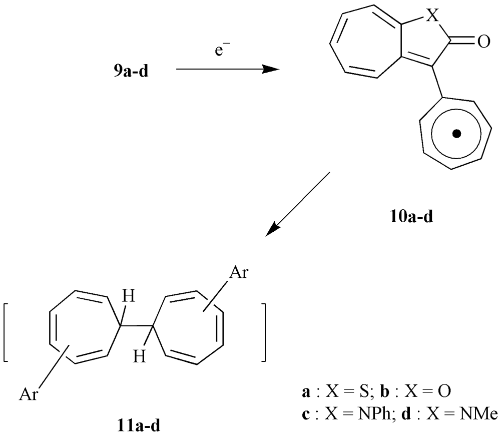
Scheme 2

Table 2 ^1H and ^{13}C NMR spectral data, pK_{R+} values and reduction potentials of tropylium ions **9a–d**, **5a,b** and **6**

	^1H NMR		^{13}C NMR					
Compd.	δ_{av} [a]	$\Delta\delta_{av}$ [b]	δ_{av} [a]	$\Delta\delta_{av}$ [b]	pK_{R+} [c]	$E1_{red}$ [d]	Bond length/Å [e]	Dihedral angle (θ/°) [e]
9a	9.00	−0.26	155.0	−1.2	3.2	−0.49	1.44	38.7
9b	8.90	−0.36	152.7	−3.5	3.8	−0.50	1.41	24.6
9c	8.79	−0.47	151.6	−4.6	5.3	−0.65	1.39	13.7
9d	8.72	−0.54	151.1	−5.1	5.7	−0.66	1.39	15.4
5a [f]	—	—	—	—	3.9	—	—	—
5b [f]	—	—	—	—	4.6	—	—	—
6 [f]	9.26	—	156.2	—	3.9	−0.51	—	—

[a] Average chemical shift of the tropylium moiety. [b] The difference from the average chemical shift of tropylium ion. [c] Measured in 50% aqueous CH_3CN. [d] Cathodic peak potential; V *vs.* Ag/Ag$^+$. [e] Bond between C3–C1′ (Fig. 3). [f] Ref. 7.

The reduction potentials of cations **9a–d** were determined by cyclic voltammetry (CV) in CH_3CN. The reduction waves of **9a–d** were irreversible under the conditions of the CV measurements; the peak potentials ($E1_{red}$) are summarized in Table 2 along with that of the reference compound **6**.[7] The ($E1_{red}$) values of cations **9a,b** are more positive, while those of **9c,d** are more negative than that of **6**. This feature suggests that cations **9a,b** are less stable, while cations **9c,d** are more stable than **6**. The irreversible nature is probably due to the formation of tropyl radicals **10a–d** and their dimerization giving **11a–d** (Scheme 3). This reduction behavior seems to be a typical property of the tropylium cation.[15]



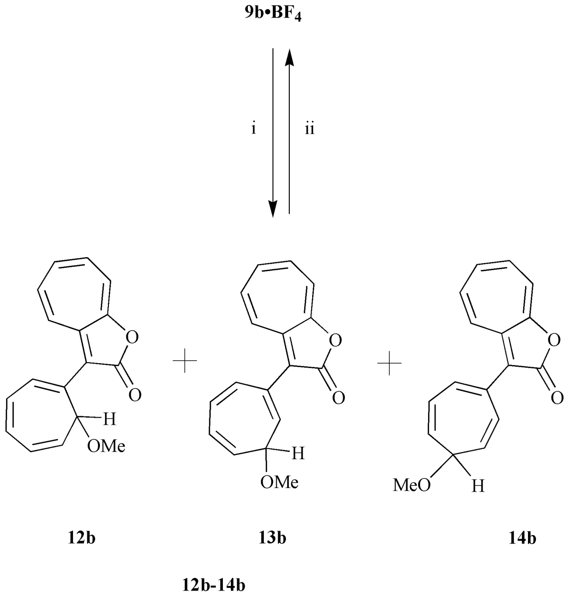
Scheme 3

The affinity of the carbocation toward the hydroxide ion, expressed by the pK_{R+} value, is the most common criterion of carbocation stability.[16] The pK_{R+} values of the cations **9a–d** are obtained spectrophotometrically and are summarized in Table 2, together with those of the reference compounds, phenyl-substituted tropylium cations **5a,b** and **6**.[7] The equilibrium of the reaction of the hydroxide ion with **9a–d** is not completely reversible. This feature is ascribed to the instability of neutralized products under the conditions of the pK_{R+} measurement. Immediate (after 5 s) acidification of an alkaline solution (*ca.* pH 14) of **9a–d** with TFA regenerated the absorption maxima of the cations in the visible regions in 56–87% yield. In order to investigate the neutralized product, the reaction of **9b** with NaOMe was carried out (Scheme 4). The product is a mixture of MeO-incorporated regioisomers **12b–14b** (in a ratio of 15 : 34 : 51; 78% yield), which were identified on the basis of the spectroscopic data, and the ratio of isomers was determined by ^1H NMR spectroscopy. The results show that the methoxide ion attacks the tropylium-unit of **9b** mainly, and not the carbonyl carbon in the five-membered ring of **9b**. Furthermore, the mixture of **12b–14b** regenerated **9b** in good yield upon treatment with aq. HBF_4 in Ac_2O. The heteroazulene-units **4a,b** do not stabilize the tropylium ion; however, **4c,d** effectively stabilize the tropylium ion. Thus, the pK_{R+} values of **9a,b** are lower by 0.7 and 0.1 pH units, respectively, than those of tropylium ion **6** and phenyl-substituted tropylium ion **5a**, while those of **9c,d** are remarkably higher by 1.4 and 1.8 pH units, respectively, than those of **5a** and **6** (Table 2). The pK_{R+} values of **9c,d** are even larger than that of 4-methoxyphenyltropylium ion **5b**. The order of pK_{R+} values of cations **9a–d** is rationalized on the basis of the energy levels of HOMOs and LUMOs of heteroazulene-units **4a–d**, which are obtained by *ab initio* MO calculations with the 6-31G* basis set of the B3LYP levels[17] in the order **9a** < **9b** < **9c** < **9d**, and they are summarized in Table 3, together with the oxidation potentials obtained by CV. The calculated HOMO energy levels of **4a,b** are much lower than those of **4c,d**, and they correlate well with the oxidation potentials obtained by CV, respectively. Since interaction between the heteroazulene unit and the tropylium ion moiety would depend on the HOMO energy levels (heteroazulene-unit) toward the tropylium ion, thus the contribution of the canonical structures

Table 3 Energy levels of HOMO and LUMO and oxidation potentials of **4a–d**.

	Energy level		CV [a]
Compd.	HOMO/eV	LUMO/eV	$E1_{ox}$/V
4a	−5.83	−2.32	+1.18
4b	−5.79	−2.18	+1.13
4c	−5.47	−1.83	+0.91
4d	−5.44	−1.77	+0.83

[a] Anodic peak potential, V *vs.* Ag/Ag$^+$.



Scheme 4 *Reagents and conditions*: i, NaOMe, MeOH, rt; ii, 42% aq. HBF_4, Ac_2O.

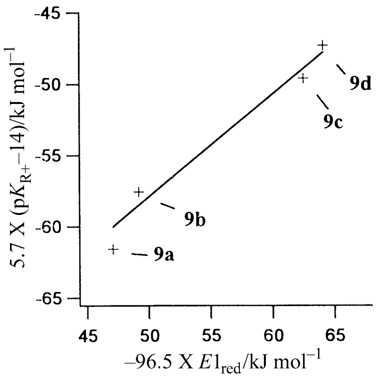


Fig. 4 Plot of pK_{R+} values against $E1_{red}$ values of **9a–d**.

B and **C** on **9a–d** becomes more important in the order **9a** < **9b** << **9c** < **9d**. This feature is also in good accordance with the spectroscopic data obtained by ^{1}H and ^{13}C NMR spectra and the stable conformation obtained by AM1 method (Table 2, Fig. 3).

The pK_{R+} values of cations **9a–d** are plotted against the $E1_{red}$ values of these cations in Fig. 4. The units of the $E1_{red}$ and pK_{R+} values have been converted to kJ mol^{-1} [$-96.5 \times E1_{red}$/V and $5.7 \times (\mathrm{p}K_{R+} - 14)$].[2,7] A linear correlation was obtained, and the slope and y-intercept of this regression line were 0.72 and −93.94, respectively (correlation coefficient = 0.984). The slope is smaller than 1.0. Thus, this feature shows that the more stable cation gives a less stable radical in single-electron reduction of **9a–d**. We have previously reported a similar correlation for cations **1a–c**, **2a–e** and **3a–e**, where the slope and y-intercept obtained were 0.72 and −48.35, respectively.[2] The slopes of the two regression lines obtained for **1a–c**[1] and **9a–d** are similar. This feature suggests that the cations **9a–d** and **1a–c** are stabilized in a similar manner.

In summary, simple synthesis and properties of a novel type of (heteroazulene-3-yl)tropylium ion **9a–d** were studied. The stability of **9a–d** was examined by reduction potentials measured by CV and by pK_{R+} values. The ^{1}H and ^{13}C NMR spectral data clearly suggested electronic contribution of the heteroazulene unit. The calculated energy levels of HOMOs are in the order **4a** < **4b** < **4c** < **4d**, and the heteroazulene unit can stabilize the tropylium ion in the order **4a** < **4b** < **4c** < **4d**. A good linear correlation between pK_{R+} values and reduction potentials ($E1_{red}$) of **9a–d** was obtained. This regression line has a similar slope to that of **1a–c**.

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 abbreviation, Trp, in the NMR spectra denotes tropyl and tropylium moieties of **7a–d** and **9a–d**. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. Values of *E* are given in units of dm^3 mol^{-1} cm^{-1}. The heteroazulenes, 2*H*-cyclohepta[*b*]thiophen-2-one **4a**,[12] 2*H*-cyclohepta[*b*]furan-2-one **4b**,[4] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **4c**[5] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **4d**[6] were prepared as described previously.

General procedure for the synthesis of heteroazulene-substituted tropyridenes 7a–d

A solution of heteroazulene **4a–d** (1 mmol), tropylium tetrafluoroborate **6** (1 mmol) and triethylamine (2 mmol) in CH_3CN (20 cm^3) was stirred at rt for 1 h. After the reaction was completed, the reaction mixture was concentrated *in vacuo*. The residue 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 SiO_2 using hexane–AcOEt (1 : 1) as the eluent to give the products **7a–d**. The results are summarized in Table 2.

For 7-(2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)cyclohepta-1,3,5-triene **7a**. Orange needles; mp 147–148 °C (from EtOH); δ_H 3.11 (1H, t, *J* 5.3, Trp-7), 5.40 (2H, dd, *J* 9.2, 5.3, Trp-1,6), 6.26 (2H, dd, *J* 9.2, 5.4, Trp-2,5), 6.70 (2H, dd, *J* 10.5, 5.4, Trp-3,4), 6.79–6.83 (1H, m, H-6), 6.86–6.91 (2H, m) 7.29–7.31 (2H, m); δ_C 37.1, 125.0, 125.4, 129.0, 129.5, 129.8, 131.0, 131.1, 131.3, 132.5, 150.6, 151.9, 189.2; ν_{max} (KBr)/cm^{-1} 1643; *m*/*z* (FAB) 253 (M$^+$ + 1) (Found: C, 75.0; H, 4.8. $C_{16}H_{12}OS\cdot\frac{1}{4}H_2O$ requires C, 74.82; H, 4.91%).

For 7-(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)cyclohepta-1,3,5-triene **7b**. Yellow prisms; mp 106–107 °C (lit.[17] 108–110 °C); δ_H 2.80 (1H, t, *J* 5.5, Trp-7), 5.48 (2H, dd, *J* 8.8, 5.5, Trp-1,6), 6.28 (2H, ddd, *J* 8.8, 3.9, 2.6, Trp-2,5), 6.74 (2H, dd, *J* 3.9, 2.6, Trp-3,4), 6.72–6.76 (1H, m, H-6), 6.90–6.96 (3H, m, H-5, 7, 8), 7.12 (1H, d, *J* 11.6, H-4); δ_C 35.2, 112.1, 112.9, 123.1, 125.3, 126.3, 130.0, 131.2, 132.4, 134.4, 148.0, 157.6, 168.8.

For 7-(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)-cyclohepta-1,3,5-triene **7c**. Yellow prisms; mp 145–146 °C (from EtOH); δ_H 3.09 (1H, t, *J* 5.5, Trp-7), 5.61 (2H, dd, *J* 8.8, 5.5, Trp-1,6), 6.28 (2H, ddd, *J* 8.8, 3.8, 2.6, Trp-2,5), 6.74 (1H, d, *J* 9.2, H-8), 6.75 (2H, dd, *J* 3.8, 2.6, Trp-3,4), 6.79 (1H, dd, *J* 10.9, 8.5, H-6), 6.91 (1H, dd, *J* 10.9, 9.2, H-7), 6.96 (1H, dd, *J* 11.3, 8.5, H-5), 7.38 (2H, d, *J* 8.4, Ph-2,6), 7.44 (1H, d, *J* 11.3, H-4), 7.48 (1H, t, *J* 7.4, Ph-4), 7.56 (2H, dd, *J* 8.4, 7.4, Ph-3,5); δ_C 35.8, 112.1, 115.7, 124.8, 124.9, 126.7, 128.5, 128.6, 128.6, 129.4, 130.7, 131.0, 131.0, 134.4, 141.0, 145.3, 168.1; ν_{max} (KBr)/cm^{-1} 1663; *m*/*z* (FAB) 312 (M$^+$ + 1) (Found: C, 84.6; H, 5.3; N, 4.5. $C_{22}H_{17}NO$ requires C, 84.86; H, 5.50; N, 4.50%).

For 7-(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)-cyclohepta-1,3,5-triene **7d**. Yellow prisms; mp 133–134 °C (from EtOH); δ_H 3.04 (1H, t, *J* 5.4, Trp-7), 3.59 (3H, s, Me), 5.54 (2H, dd, *J* 8.7, 5.4, Trp-1,6), 6.26 (2H, ddd, *J* 8.7, 3.5, 2.9, Trp-2,5), 6.74 (2H, dd, *J* 3.5, 2.9, Trp-3,4), 6.86 (1H, d, *J* 8.6, H-8), 6.81 (1H, dd, *J* 10.9, 8.6, H-6), 6.93 (1H, dd, *J* 11.2, 8.6, H-5), 7.05 (1H, dd, *J* 10.9, 8.6, H-7), 7.37 (1H, d, *J* 11.2, H-4); δ_C 26.4, 35.7, 110.5, 116.2, 124.8, 125.0, 126.3, 128.0, 130.3, 130.4, 131.0, 140.5, 144.7, 168.3; ν_{max} (KBr)/cm^{-1} 1664; *m*/*z* (FAB) 250 (M$^+$ + 1) (Found: C, 81.7; H, 5.9; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.90; H, 6.06; N, 5.62%).

General procedure for the synthesis of heteroazulene-substituted tropylium ions 9a–d·BF$_4$

A solution of **7a–d** (0.20 mmol) in xylene (5 cm^3) was heated under reflux for 1 h and concentrated *in vacuo*. To the residue 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. After evaporation of the CH_2Cl_2, the residue was dissolved in a mixture of acetic anhydride (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 **9a–d·BF$_4$**$^-$. The results are summarized in Table 1.

For (2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)tropylium tetrafluoroborate **9a·BF$_4$**$^-$. Dark brown needles; mp 170–171 °C (from CH_3CN–Et_2O); δ_H (CD_3CN) 7.57–7.66 (3H, m, H-4, 5, 7), 8.10–8.14 (2H, m, H-6, 8), 8.84–8.88 (2H, m, Trp-3), 8.90–8.94 (2H, m, Trp-4), 9.22 (2H, d, *J* 10.2, Trp-2); δ_C (CD_3CN) 124.8 (C-3), 130.8 (C-8), 137.2 (C-4), 137.8 (C-6), 140.2 (C-7), 141.2 (C-5), 153.2 (C-8a), 153.3 (Trp-3,4), 154.6 (Trp-2), 157.0 (C-3a), 163.1 (Trp-1), 186.7 (C=O); ν_{max} (KBr)/cm^{-1} 1617, 1084; λ_{max} (CH_3CN)/nm (log ε) 556 (4.05), 427 (3.66), 399 (3.63), 305 (4.22), 276 (4.24), 229 (4.36), 205 (4.34); *m*/*z* (FAB) 251 (M$^+$ − BF_4) (Found: M$^+$ − BF_4, 251.0562. $C_{16}H_{11}BF_4OS$

requires M − BF_4, 251.0530) (Found: C, 56.9; H, 3.0. $C_{16}H_{11}BF_4OS$ requires C, 56.83; H, 3.28%).

For (2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)tropylium tetrafluoroborate **9b·BF$_4$$^-$**. Dark brown powder; mp 189–190 °C (from CH_3CN–Et_2O); δ_H (CD_3CN) 7.81 (1H, dd, *J* 9.4, 9.0, H-6), 7.93–8.03 (1H, m, H-5,7,8), 8.56 (1H, d, *J* 11.0, H-4), 8.64 (2H, dd, *J* 9.7, 8.9, Trp-4), 8.75 (2H, dd, *J* 10.8, 8.9, Trp-3), 9.31 (2H, d, *J* 10.8, Trp-2); δ_C (CD_3CN) 106.8 (C-3), 124.4 (C-8), 130.2 (C-4), 139.5 (C-6), 141.3 (C-7), 144.1 (C-5), 149.6 (Trp-2), 151.3 (Trp-4), 152.0 (Trp-3), 152.3 (C-8a), 161.3 (C-3a), 162.8 (Trp-1), 166.7 (C=O); ν_{max} (KBr)/cm^{-1} 1744, 1256, 1084; λ_{max} (CH_3CN)/nm (log ε) 538 (4.59), 359 (3.74), 264 (4.35), 223 (4.46); MS (FAB) 235 (M^+ − BF_4) (Found: M^+ − BF_4, 235.0779. $C_{16}H_{11}BF_4O_2$ requires M − BF_4, 235.0759) (Found: C, 59.7; H, 3.2. $C_{16}H_{11}BF_4O_2$ requires C, 59.67; H, 3.44%).

For (1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)tropylium tetrafluoroborate **9c·BF$_4$$^-$**. Green needles; mp 165–166 °C (from CH_3CN–Et_2O); δ_H (CD_3CN) 7.46 (2H, d, *J* 8.4, Ph-2,6), 7.65 (1H, t, *J* 7.2, Ph-4), 7.56 (1H, d, *J* 10.0, H-8), 7.69 (2H, dd, *J* 8.4, 7.2, Ph-3,5), 7.75 (1H, dd, *J* 10.1, 9.2, H-6), 7.84 (1H, dd, *J* 10.1, 10.0, H-7), 7.95 (1H, dd, *J* 11.0, 9.2, H-5), 8.42 (2H, dd, *J* 9.8, 9.1, Trp-4), 8.56 (2H, dd, *J* 10.8, 9.1, Trp-3), 8.76 (1H, d, *J* 11.0, H-4), 9.40 (2H, d, *J* 10.8, Trp-2); δ_C (CD_3CN) 111.3 (C-3), 122.8 (C-8), 129.4 (Ph), 130.0 (C-4), 130.9 (Ph), 131.1 (Ph), 134.4 (Ph), 137.8 (C-6), 140.6 (C-7), 141.2 (C-5), 146.6 (C-8a), 148.9 (Trp-2), 149.5 (Trp-4), 150.4 (Trp-3), 151.1 (C-3a), 163.8 (Trp-1), 166.5 (C=O); ν_{max} (KBr)/cm^{-1} 1676, 1084; λ_{max} (CH_3CN)/nm (log ε) 567 (4.58), 375 (3.64), 304 (4.24), 271 (4.27), 234 (4.48); *m*/*z* (FAB) 310 (M^+ − BF_4) (Found: M^+ − BF_4, 310.1204. $C_{22}H_{16}BF_4NO$ requires M − BF_4, 310.1207) (Found: C, 64.8; H, 4.0; N, 3.7. $C_{22}H_{16}BF_4NO\cdot\frac{1}{2}H_2O$ requires C, 65.05; H, 4.22; N, 3.45%).

For (1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)tropylium tetrafluoroborate **9d·BF$_4$$^-$**. Dark brown powder; mp 198–199 °C (from CH_3CN–Et_2O); δ_H (CD_3CN) 3.63 (3H, s, Me), 7.77 (1H, dd, *J* 10.3, 9.7, H-6), 7.89 (1H, d, *J* 10.1, H-8), 7.93 (1H, dd, *J* 10.4, 9.7, H-5), 8.02 (1H, dd, *J* 10.3, 10.1, H-7), 8.34 (2H, dd, *J* 9.8, 9.2, Trp-4), 8.48 (2H, dd, *J* 10.6, 9.2, Trp-3), 8.69 (1H, d, *J* 10.4, H-4), 9.34 (2H, d, *J* 10.4, Trp-2); δ_C (CD_3CN) 27.9 (Me), 111.4 (C-3), 122.2 (C-8), 129.7 (C-4), 137.2 (C-6), 140.5 (C-7), 141.0 (C-5), 146.2 (C-8a), 148.1 (Trp-2), 148.9 (Trp-4), 149.9 (Trp-3), 150.9 (C-3a), 163.6 (Trp-1), 166.5 (C=O); ν_{max} (KBr)/cm^{-1} 1685, 1058; λ_{max}(CH_3CN)/nm (log ε) 567 (4.58), 375 (3.76), 306 (4.35), 274 (4.32), 234 (4.49); *m*/*e* (FAB) 248 (M^+ − BF_4) (Found: M^+ − BF_4, 248.1035. Calcd for $C_{17}H_{14}NO$ − BF_4, 248.1039) (Found: C, 61.4; H, 3.9; N, 4.6. Calcd for $C_{17}H_{14}BF_4NO$: C, 60.93; H, 4.21; N, 4.18%).

Reaction of (2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)tropylium tetrafluoroborate 9b·BF$_4$$^-$ with NaOMe

Sodium (4 mmol) was dissolved in methanol (20 cm^3) and **9b·BF$_4$$^-$** (1 mmol) was added to this solution. The mixture was stirred at rt for 1 h and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al_2O_3 using hexane–AcOEt (1 : 1) as the eluent to give a mixture of isomers **12b**, **13b** and **14b** in a ratio of 15 : 34 : 51 (78%).

For a mixture of **12b**, **13b** and **14b**: orange oil; ν_{max} ($CHCl_3$)/cm^{-1} 1740, 1267; *m*/*z* (FAB) 235 (M^+ − OMe) (Found: M^+ − OMe, 235.0798. $C_{17}H_{14}O_3$ requires M – OMe, 235.0759); δ_C 55.5, 56.6, 56.8, 75.2, 78.0, 110.2, 110.5, 111.0, 113.6, 113.8, 113.8, 122.7, 123.2, 123.3, 124.0, 124.3, 124.4, 125.4, 126.2, 127.0, 127.0, 127.3, 127.4, 127.6, 127.7, 128.1, 129.8, 130.8, 131.0, 131.0, 131.1, 131.3, 131.8, 132.1, 132.5, 132.6, 132.7, 134.8, 134.8, 134.9, 146.9, 147.0, 147.3, 157.4, 157.4, 157.5, 167.4, 167.8, 168.0 (two carbons overlapping). For **12b** δ_H 3.20 (3H, s, OMe), 4.56 (1H, d, *J* 7.2, Trp-7), 5.87 (1H, dd, *J* 10.0, 7.2, Trp-6), 6.52 (1H, dd, *J* 10.0, 6.3, Trp-5), 6.75–6.99 (7H, m, H-5, 6, 7, 8, Trp-2, 3, 4), 7.29 (1H, d, *J* 11.4, H-4). For **13b** δ_H 3.47 (1H, t, *J* 4.8, Trp-7), 3.50 (3H, s, OMe), 5.60–5.65 (1H, m, Trp-6), 5.91 (1H, d, *J* 4.8, Trp-1), 6.20 (1H, dd, *J* 9.7, 4.8, Trp-5), 6.75–6.99 (6H, m, H-5, 6, 7, 8, Trp-3, 4). For **14b** δ_H 3.48 (3H, s, OMe), 3.54 (1H, t, *J* 4.7, Trp-7), 5.60–5.65 (2H, m, Trp-1, 6), 6.28 (1H, dd, *J* 10.0, 6.9, Trp-5), 6.33 (1H, d, *J* 10.0, Trp-2), 6.75–6.99 (4H, m, H-5, 6, 7, 8), 7.29 (1H, d, *J* 6.9, Trp-4), 7.54 (1H, d, *J* 11.4, H-4).

Reaction of a mixture of 12b, 13b and 14b with HBF$_4$

A mixture of **12b–14b** (0.25 mmol) was dissolved in a mixture of acetic anhydride (5 cm^3) and aq. 42% HBF_4 (1 cm^3), and the mixture was stirred at 0 °C for 1 h. To the mixture was added Et_2O (100 cm^3) and the precipitates were collected by filtration to give **9b·BF$_4$$^-$** (81%).

Determination of pK_{R+} value of tropylium ions 9a–d

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 2.2–4.0) and potassium hydrogen phthalate (0.1 M) and NaOH (0.1 M) (for pH 4.1–5.9) in various portions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 2–4 mg of cation **9a–d·BF$_4$$^-$** in CH_3CN (20 cm^3), were diluted to 10 ml with the buffer solution (5 cm^3) and CH_3CN (4 cm^3). The UV–vis spectrum was recorded for each cation **9a–d** 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 (546 nm for **9a**; 532 nm for **9b**; 556 nm for **9c**; 556 nm for **9d**) of each cation was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

Cyclic voltammetry of heteroazulenes 4a–d and tropylium ions 9a–d

The reduction potentials of **4a–d** and **9a–d** 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 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 results are summarized in Tables 2 and 3.

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