

# Synthesis, Stability, and Spectroscopic and Electronic Properties of Three Benzocyclohepta[a]azulenylium Ions<sup>1</sup>

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Received February 26, 2002

Novel  $\pi$ -systems, three benzocyclohepta[a]azulenylium ions,  $7\mathbf{a}-\mathbf{c}$ , are synthesized, and their stability and properties have been characterized in terms of the position of the benzo-annulation and compared with those of the parent cyclohepta[a]azulenylium ion 4. Benzocyclohepta[6,7-a]azulenylium ion (7a) (p $K_{R^+}$  = 7.3,  $\hat{E}_{red}$  = -0.567 V vs Ag/Ag<sup>+</sup>) and benzocyclohepta[6,5-*a*]azulenylium ion (7b)  $(pK_{R^+} = 5.1, E_{red} = -0.482 \text{ V vs Ag/Ag^+})$ , which are annulated with benzene on the position having a high bond order of 4, are not appreciably destabilized compared with cyclohepta[a]azulenylium ion (4) (p $K_{R^+}$  = 7.3,  $E_{red}$  = -0.458 V vs Åg/Åg<sup>+</sup>). On the other hand, benzocyclohepta-[7,6-*a*]azulenylium ion (7c) ( $pK_{R^+} = 1.6$ ,  $E_{red} = -0.197$  V vs Ag/Ag<sup>+</sup>) is considerably destabilized, probably due to enhanced contribution of the quinoid structure of the benzene ring, which is annulated on the position having a low bond order of the cyclohepta[a]azulenylium ion moiety. Furthermore, the cations 7a and 7b are more stable than 12,13-dihydrobenzocyclohepta[7,6-a]azulenylium ion (25) (p $K_{R^+}$  = 4.8,  $E_{red}$  = -0.513 V vs Ag/Ag<sup>+</sup>), which is a dihydrogenated compound of 7a, while 7c is less stable than 25. These features are reflected in the considerable red shift of the longest absorption maximum of the electronic spectrum of 7c, as compared with those of 4, 7a, and **7b**, and in the chemical shifts of the protons and their coupling constants of the <sup>1</sup>H NMR spectra. Furthermore, the <sup>1</sup>H NMR spectra and electronic spectra of 5H-benzocyclohepta[6,7-a]azulen-5-one (8a) and 7H-benzocyclohepta[6,5-a]azulen-7-one (8b) in acidic media have also been studied to clarify the spectral characteristics similar to those of **7a** and **7b**.

# Introduction

The  $\pi$ -conjugation mode in polycyclic conjugated  $\pi$ -systems containing more than one (4n + 2) conjugation loop is an important subject from both theoretical and experimental viewpoints. Combination of more than one  $\pi$ -system can endow new properties to the original  $\pi$ -system. Previously, we have studied the synthesis and structural and chemical properties of catacondensed aromatic  $\pi$ -systems azuleno[1,2-*a*]azulene<sup>2</sup> and its 6-aza and 6,7-diaza analogues<sup>3</sup> and 1-azaazuleno- and azuleno-annulated 1,6-methano[10]annulenes.<sup>4</sup> In this connection, we have now focused our attention on the cycloheptatrienylium (tropylium) ion (1) (Figure 1), which is a representative of the nonbenzenoid aromatic  $6\pi$ -electron system, and it has a fairly thermodynamic stability (p $K_{R^+} = 3.9^5$  or  $4.8^6$ ). While the tropylium ion is destabilized by benzo-annu-



### FIGURE 1.

lation as demonstrated by benzotropylium ion (2) (p $K_{R^+}$  = 1.6)<sup>7</sup> and dibenzotropylium ion (3) (p $K_{R^+}$  = -3.7),<sup>8</sup> a

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<sup>(1)</sup> This paper was presented at the National Meeting of the Chemical Society of Japan, Niigata, October 1992; Abstract No. 4A723; Tokyo, March, 1993; Abstract No. 3B434.

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tropylium ion annulated with azulene, cyclohepta[a]azulenylium ion (4) (Figure 1), has been synthesized and clarified to be appreciably stabilized (p $K_{R^+} = 7.3$ ).<sup>9</sup> The stabilizing extent of the azulene annulation onto the tropylium ion is similar to that of tropylium ions annulated with five-membered aromatic heterocycles 5 ( $pK_{R^+}$ = 6.7) and **6** (p $K_{R^+}$  = 6.0) (Figure 1).<sup>10</sup> The azulene also stabilizes cations attached at the 1-position as suggested by theoretical calculations,<sup>11</sup> a large dipole moment,<sup>12</sup> and the demonstrated remarkable stability of the tri(azulen-1-yl)methylium ion (p $K_{\mathbb{R}^+} = 11.3$ ), di(azulen-1-yl)phenylmethylium ion (p $K_{R^+}$  = 10.5), and azulen-1-yldiphenylmethylium ion  $(pK_{R^+} = 3.0)^{13}$  as compared with the triphenylmethylium ion (p $K_{R^+} = -6.4$ ).<sup>14</sup> Furthermore, since the resonance energy of benzene (25.9 kcal mol<sup>-1</sup>) is larger than that of azulene  $(12.8 \text{ kcal mol}^{-1})$ ,<sup>15</sup> the  $\pi$ -conjugation loop of benzene should perturb the azulenoannulated tropylium (cyclohepta[a]azulenylium) ion (4). Regarding the <sup>1</sup>H NMR spectrum of 4 (Table 2, vide infra),<sup>16</sup> the existence of a bond-length alternation is suggested by the coupling constants, as well as the theoretical calculation.<sup>17</sup> Since the correlation between bond lengths and coupling constants in the sevenmembered ring of azulene<sup>18</sup> has been clarified, the bond orders of C1–C2 (or C9–C10) ( $J_{1-2} = 10.3$  Hz) and C3– C4 (or C7–C8) ( $J_{3-4} = 10.3$  Hz) seem to be larger as compared with those of C2–C3 (or C8–C9) ( $J_{2-3} = 9.4$ Hz) and C4–C5 (or C6–C7) ( $J_{4-5} = 9.4$  Hz) in compound 4. Thus, it is interesting to investigate how the conjugation mode as well as the thermodynamic stability ( $pK_{R^+}$ value) is affected by the position of the benzo-annulation. We studied the synthesis of new  $\pi$ -systems benzocyclohepta[6,7-a]azulenylium ion (7a), benzocyclohepta[6,5a]azulenylium ion (7b), and benzocyclohepta[7,6-a]azulenylium ion (7c) (Figure 1) and their thermodynamic stability. Furthermore, the synthesis and properties of 5H-benzocyclohepta[6,7-a]azulen-5-one (8a) and 7H-benzocyclohepta[6,5-a]azulen-7-one (8b) (Figure 1)in acidic media have also been studied. We describe the results in detail here.

# **Results and Discussion**

Synthesis of Benzocyclohepta[a]azulenylium Tet**rafluoroborates** 7a-c·BF<sub>4</sub><sup>-</sup>. Preparation of three types of benzocyclohepta[a]azulene skeletons was performed by application of an efficient enamine method of azulene synthesis, which consists of the cycloaddition reaction of enamines with 2H-cyclohepta[b]furan-2-one (9),<sup>19</sup> ex-

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plored by Takase, Yasunami, and their co-workers.<sup>20a-e</sup> Pyrrolidinoenamine 11, which was prepared in situ from 5,6,8,9-tetrahydro-7*H*-benzocyclohepten-7-one (10)<sup>21</sup> and pyrrolidine in the usual manner, was allowed to react with 9 to give azulene 13 in good yield (Scheme 1). This azulene synthesis is considered to proceed via an intermediate, 12, which derives from cycloaddition via a stepwise fashion.<sup>20</sup> In a similar fashion, the enamine **15**, which derives from 6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one (14)<sup>22</sup> and pyrrolidine, reacted with 9 to yield azulene 16 in moderate yield. On the other hand, the reaction of 5,7,8,9-tetrahydro-6H-benzocyclohepten-6-one  $(17)^{23}$  with pyrrolidine was expected to give an isomeric mixture of two enamines, 18 and 19; however, the reaction of the enamines with 9 afforded azulenoid compound **20**, which derives from the isomer **19**, and the expected compound **20**' was not obtained. The results are summarized in Table 1. In the azulene synthesis, the product ratio is not dependent on the composition of isomeric enamines, but is dependent on the reactivity of the isomeric enamines.<sup>24</sup> According to the AM1 method,<sup>25</sup> the heat of formation ( $\Delta H_{\rm f}^{\circ}$ ) for **18** and **19** is predicted to be 28.00 and 30.81 kcal mol<sup>-1</sup>, and the energy levels of the HOMOs for these isomers are estimated to be -8.02and -8.22 eV, respectively (Figure 2). Furthermore, the difference in the coefficients of the HOMOs at the  $\beta$ -carbon atoms for the enamine moieties of **18** and **19** is small. The reaction of 18 (having a higher HOMO) with 9 would experience a large steric hindrance between the hydrogen atom at the peri position and the sevenmembered ring of 9, however, and thus, the enamine 18 would not afford 20', but the enamine 19 would intervene in the reaction with 9 to give 20 albeit in modest yield. According to a convenient procedure for introduction of a carbonyl function in azulenoid compounds,<sup>26</sup> 13, 16, and 20 were treated with DDQ in moist acetone to afford carbonyl compounds 21, 22, and 23 in good yield, respectively (Scheme 2). The spectroscopic characteristics for new compounds 13, 16, and 20–23 were satisfactory for the assigned structures.

Compound 21 was dehydrogenated with DDQ in 1,4dioxane under reflux to give 5H-benzocyclohepta[6,7-a]azulen-5-one (8a) in modest yield (Scheme 3). The carbonyl function of compound 8a was reduced easily

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<sup>(16) &</sup>lt;sup>13</sup>C NMR (125.8 MHz, CD<sub>3</sub>CN) δ 125.0, 135.5, 138.6, 142.7, 143.1, 143.7, 147.4, 153.7.

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# SCHEME 1



with NaBH<sub>4</sub> in the presence of CeCl<sub>3</sub>·7H<sub>2</sub>O<sup>27</sup> to give 5*H*benzocyclohepta[6,7-*a*]azulene (**24**) in good yield. Direct formation of hydrocarbon **24**, but not alcohol, from carbonyl compound **8a** is probably due to the formation of the stable cationic intermediate **7a** by the elimination of  $-\text{OCeX}_n$ . Hydride abstraction of **24** with trityl tetrafluoroborate (TrBF<sub>4</sub>)<sup>28</sup> easily proceeded to result in the formation of benzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate (**7a**·BF<sub>4</sub><sup>-</sup>). Upon treatment with TrBF<sub>4</sub>, com-

TABLE 1. Results for the Reactions of 9 with Enamines11 and 15 and a Mixture of 18 and 19

enamine	solvent	amt of <b>9</b> ª	reaction time/h <sup>b</sup>	product (yield/%)
<b>11</b> <sup>c</sup>	EtOH	0.5	8	<b>13</b> (85) <sup>d</sup>
$15^d$	BuOH	2.0	37	16 (77) <sup>e</sup>
<b>18</b> and <b>19</b> <sup><i>e</i></sup>	BuOH	1.2	25	<b>20</b> (39) <sup>e</sup>

<sup>*a*</sup> Molar ratio of **9** toward the original ketones **10**, **14**, and **17**. <sup>*b*</sup> Heated under reflux. <sup>*c*</sup> Prepared in situ by using **10** (1.02 g, 6.4 mmol), pyrrolidine (4.4 g, 62 mmol), and TsOH·H<sub>2</sub>O (64 mg, 0.34 mmol) in toluene (20 mL); refluxed for 7 h. <sup>*d*</sup> Prepared in situ by using **14** (1.33 g, 8.3 mmol), pyrrolidine (3.56 g, 50 mmol), and TsOH·H<sub>2</sub>O (33 mg, 0.17 mmol) in benzene (20 mL); refluxed for 18 h. <sup>*e*</sup> Prepared in situ by using **17** (1.29 g, 8.06 mmol), pyrrolidine (3.75 g, 53 mmol), and TsOH·H<sub>2</sub>O (67 mg, 0.35 mmol) in benzene (24 mL); refluxed for 18 h. <sup>*d*</sup> Based on **9**. <sup>*e*</sup> Based on benzocycloheptanone.



**FIGURE 2.** Coefficients and energy levels of HOMOs and heat of formation  $(\Delta H_{\rm f}^{\circ})$  for isomeric enamines **18** and **19**.





pound **13** was also converted to 12,13-dihydrobenzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate (**25**·BF<sub>4</sub><sup>-</sup>). The cations **7a** and **25** were easily reduced with NaBH<sub>4</sub> to regenerate **24** and **13**, respectively. In a similar fashion, dehydrogenation of **22** with DDQ afforded 7*H*-benzocyclohepta[6,5-*a*]azulen-7-one (**8b**), which was reduced smoothly with NaBH<sub>4</sub> in the presence of CeCl<sub>3</sub>·7H<sub>2</sub>O<sup>27</sup> to give 7*H*-benzocyclohepta[6,5-*a*]azulen[6,5-*a*]azulene (**26**) in good yield, while compound **27** was not isolated (Scheme 4). Hydride abstraction of **26** with TrBF<sub>4</sub> gave benzocyclohepta[6,5-*a*]azulenylium tetrafluoroborate (**7b**·BF<sub>4</sub><sup>-</sup>). On the other hand, after the reduction of **22** with NaBH<sub>4</sub> and CeCl<sub>3</sub>·7H<sub>2</sub>O, the resulting alcohol, which was not isolated, was subsequently treated with TsCl in pyridine to give 5*H*-benzocyclohepta[6,5-*a*]azulene (**27**) in good

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SCHEME 3



yield. Upon treatment with TrBF<sub>4</sub>, compound **27** was also converted to **7b**·BF<sub>4</sub><sup>-</sup>. The cation **7b** was reduced with NaBH<sub>4</sub> to generate a mixture of **26** and **27** in **88**% and 4% yields, respectively, as determined by <sup>1</sup>H NMR spectroscopy. Thus, the structural relationship between **26** and **27** and the salt **7b**·BF<sub>4</sub><sup>-</sup> was assessed. Similarly, the reduction of **23** with NaBH<sub>4</sub> in the presence of CeCl<sub>3</sub>. 7H<sub>2</sub>O gives an alcohol, which was subsequently treated with TsOH to afford 5*H*-benzocyclohepta[7,6-*a*]azulene (**28**) (Scheme 5). Compound **28** reacted smoothly with TrBF<sub>4</sub> to give benzocyclohepta[7,6-*a*]azulenylium tetrafluoroborate (**7c**·BF<sub>4</sub><sup>-</sup>), which regenerated **28** upon





reduction with NaBH4. Thus, the relation of  ${\bf 28}$  with  ${\bf 7c}{\bf \cdot}BF4^-$  was also assessed.

The spectroscopic characteristics for new compounds **8a,b**, **24**, and **26–28** were satisfactory for the assigned structures. The structures of salts **7a–c**·BF<sub>4</sub><sup>–</sup> and **25**·BF<sub>4</sub><sup>–</sup> were also assigned on the basis of their spectral data and elemental analyses. The characteristic bands of the counterion BF<sub>4</sub><sup>–</sup> are observed at 1036–1139 cm<sup>-1</sup> in their IR spectra. The features and the NaBH<sub>4</sub> reductions of those cations regenerating **24** and **26** and **27**, **28**, and **13**, respectively, support the cationic nature of the compounds.

Spectroscopic Properties of Benzocyclohepta[a]azulenylium Ions 7a-c. The spectroscopic characteristics of cations **7a**,**b**, which are annulated with benzene on the position having a high bond order of 4, are remarkably different from those of 7c, which is annulated with benzene on the position having a low bond order (vide supra). The <sup>1</sup>H NMR spectra of **4**, **7a**–**c**, **8a,b**, and **25** are assigned on the basis of <sup>1</sup>H–<sup>1</sup>H COSY spectra, and the <sup>1</sup>H NMR spectral data are summarized in Table 2. The average chemical shifts ( $\delta_{av}$ ) of protons H5, H12-H13 ( $\delta_{av} = 8.79$ , benzo-annulated ring) and H6–H7–H8– H9–H10 ( $\delta_{av}$  = 8.89, terminal ring) for **7a** as well as those of H5–H6–H7 ( $\delta_{av}$  = 8.61, benzo-annulated ring) and H8–H9–H10–H11–H12 ( $\delta_{av} = 8.82$ ; terminal ring) for **7b** are much lower than that of neutral azulene ( $\delta_{av}$ = 7.47),<sup>29</sup> higher than that of tropylium ion (1) ( $\delta$  = 9.26),<sup>6</sup> and similar to that of the parent cation **4** ( $\delta_{av} = 8.80$ ). Thus, the cationic nature of 7a,b is characterized. Furthermore, the average chemical shift of H6-H7-H8-H9–H10 on the terminal ring ( $\delta_{av} = 8.89$ ) is lower than that of H5, H12–H13 on the benzo-annulated ring ( $\delta_{av}$ = 8.79) for **7a**. A similar feature is observed for **7b** ( $\delta_{av}$ = 8.82, terminal ring;  $\delta_{av}$  = 8.61, benzo-annulated ring). These features suggest that the positive charges of 7a,b are delocalized more on the terminal seven-membered rings, and thus, contribution of the canonical structures 7aA and 7bA is more important as compared with 7aB and 7bB, respectively (Scheme 6). Regarding the bondlength alternations of **7a**, the coupling constant  $(J_{12-13})$ = 11.5 Hz) on the benzo-annulated ring is obviously larger than those ( $J_{6-7} = 9.0$  Hz,  $J_{7-8} = 10.2$  Hz,  $J_{8-9} =$ 8.8 Hz, and  $J_{9-10} = 10.3$  Hz) of the terminal ring, and the latter values are similar to the corresponding values

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TABLE 2. <sup>1</sup>H NMR Chemical Shifts ( $\delta$ ) and Vicinal Coupling Constants (*J*/Hz) of Benzocyclohepta[*a*]azulenylium Salts 7a-c·BF<sub>4</sub><sup>-</sup> and Those of the Related Compounds 4·BF<sub>4</sub><sup>-</sup>, 8a,b, and 25·BF<sub>4</sub><sup>- a</sup>

				-									
compd	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	H12	H13
$4 \cdot BF_4^{-b}$	9.04	8.32	8.56	8.37	9.75	(H5)	(H4)	(H3)	(H2)	(H1)	8.22		
	J=1	$0.3 \ J = 9$	$9.4 \ J=1$	$10.3 \ J=9$	9.4								
<b>7a</b> •BF₄ <sup>−</sup> <sup>b</sup>	8.29 <sup>e</sup>	8.20 <sup>e</sup>	8.12 <sup>e</sup>	8.63 <sup>e</sup>	9.85	$9.75^{e}$	$8.55^{e}$	8.60 <sup>e</sup>	8.49 <sup>e</sup>	9.04 <sup>e</sup>	8.12	8.25 01	8.28
	J =	7.9 J =	7.2 $J =$	7.8		J = 9	9.0 $J = 1$	10.2  J = 8	3.8  J=1	0.3		J=1	1.5
7 <b>b</b> •BF₄ <sup>−</sup> <sup>b</sup>	9.00 <sup>e</sup>	8.18 <sup>e</sup>	8.09 <sup>e</sup>	8.32 <sup>e</sup>	8.60	7.85	9.39	9.55	8.47 <sup>e</sup>	8.57 <sup>e</sup>	8.46 <sup>e</sup>	9.03 <sup>e</sup>	8.75
	J = 8.2 $J = 7.1$ $J = 7.9$ $J = 11.3$ $J = 8.8$ $J = 9.1$ $J = 10.5$ $J = 9.0$ $J = 10.3$												
$7c \cdot BF_4^{-c}$	8.87	8.36	8.46	8.76	10.29	f	8.97	7.96 <sup>e</sup>	8.38	8.10 <sup>e</sup>	9.87	9.98	9.34
	J =	8.5 $J =$	7.1 $J =$	8.4			J = 1	0.8 J = 9	J = 9.0	$J_{0.9}$ $J_{I}=$	8.5	J=1	0.6
$\mathbf{8a}^d$	7.64	$1-7.67^{g}$ (3	BH)	8.7-8.8 <sup>g</sup>		$10.17^{e}$	$7.68^{e}$	$7.80^{e}$	$7.48^{e}$	8.44 <sup>e</sup>	7.39	7.28 01	7.45
			·			J = 9	9.7 J = 1	0.2 J = 9	$J_{3}$ $J = 1$	0.1		J=1	1.6
8a <sup>c</sup>	8.22 <sup>e</sup>	8.18 <sup>e</sup>	8.09 <sup>e</sup>	8.84 <sup>e</sup>		10.45 <sup>e</sup>	8.36 <sup>e</sup>	8.40 <sup>e</sup>	8.27 <sup>e</sup>	8.91	f	8.01 01	8.09
	J =	7.8 $J =$	7.1 $J =$	8.5		J = 9	9.4 $J=1$	10.3  J = 8	3.7  J=1	0.3		J=1	1.5
$\mathbf{8b}^d$	8.51	7.57 <sup>e</sup>	7.63	7.69 <sup>e</sup>	7.38	6.92		10.23	7.65	7.80	7.49	8.50	7.99
	J =	7.4 J =	7.4 J =	7.7	J =	12.8		J = 9	J = 1	0.3 J =	9.3 $J =$	10.1	
<b>8b</b> <sup>c</sup>	9.00 <sup>e</sup>	8.12 <sup>e</sup>	8.02 <sup>e</sup>	8.17 <sup>e</sup>	8.35	7.60		10.42	8.28 <sup>e</sup>	8.37 <sup>e</sup>	8.23 <sup>e</sup>	8.95 <sup>e</sup>	f
	J =	8.2 $J =$	7.2 $J =$	7.8	J =	12.3		J =	9.5 $J = 1$	$10.1 \ J =$	9.2 $J =$	10.1	
<b>25</b> •BF₄ <sup>− b</sup>	$7.49^{e}$	7.65 <sup>e</sup>	$7.54^{e}$	7.93 <sup>e</sup>	8.80	9.27	8.5	$0 - 8.58^{g}$ (3)	BH)	8.78	7.52	3.22 - 3.3	34 <sup>g</sup> (4H)
	J =	7.6 $J =$	7.6 J=	7.6		J =	8.4		J =	8.3			. ,

<sup>*a*</sup> Recorded on a 400 or 500 MHz spectrometer. <sup>*b*</sup> Recorded in CD<sub>3</sub>CN. <sup>*c*</sup> Recorded in CF<sub>3</sub>CO<sub>2</sub>D. <sup>*d*</sup> Recorded in CDCl<sub>3</sub>. <sup>*e*</sup> The signals are broadened or additionally split (J = 0.5 - 2.2 Hz) by long range coupling. <sup>*f*</sup> The signals disappear because of proton-deuterium exchange. <sup>*g*</sup> The signals appear as a multiplet.

#### **SCHEME 6**



 $(J_{4-5} = 9.4 \text{ Hz}, J_{3-4} = 10.3 \text{ Hz}, J_{2-3} = 9.4 \text{ Hz}, \text{ and } J_{1-2} = 10.3 \text{ Hz})$  of the seven-membered ring in the parent cation **4**, respectively. Similarly, the difference ( $\Delta J = 2.5 \text{ Hz}$ ) in the coupling constants ( $J_{5-6} = 11.3 \text{ Hz}$  and  $J_{6-7} = 8.8 \text{ Hz}$ ) on the benzo-annulated ring of **7b** suggests an appreciable bond-length alternation, and the coupling constants ( $J_{8-9} = 9.1 \text{ Hz}, J_{9-10} = 10.3 \text{ Hz}, J_{10-11} = 9.0 \text{ Hz}$ )

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Hz, and  $J_{11-12} = 10.3$  Hz) of the terminal ring suggest the  $\pi$ -electron delocalization to be similar to that of **4**. This feature also suggests that the  $\pi$ -electron delocalization of the terminal seven-membered ring of **7a** and **7b** is much larger as compared with that of the benzoannulated ring to favor the canonical structures **7aA** and **7bA**, respectively.

On the contrary, the average chemical shift of the protons H7–H8–H9–H10–H11 ( $\delta_{av}$  = 8.66, terminal ring) is higher than that of H5, H12–H13 ( $\delta_{av} = 9.87$ , benzo-annulated ring) for 7c, suggesting the cationic nature of **7c** and that the positive charge is delocalized more on the benzo-annulated ring to characterize the important contribution of the canonical structure 7cB as compared with **7cA**. The coupling constant ( $J_{12-13} = 10.6$ Hz) on the benzo-annulated ring of 7c is smaller than that of the benzo-annulated rings of **7a** ( $J_{12-13} = 11.5$  Hz) and close to the average ( $J_{\rm av} = 10.1$  Hz) of **7b** ( $J_{5-6} = 11.3$  Hz and  $J_{6-7} = 8.8$  Hz), suggesting a  $\pi$ -electron delocalization of the benzo-annulated ring. Regarding the coupling constants ( $J_{7-8} = 10.8$  Hz,  $J_{8-9} = 9.0$  Hz,  $J_{9-10}$ = 9.9 Hz, and  $J_{10-11}$  = 8.5 Hz) of the terminal ring of 7c, bond-length alternation of the ring seems to be larger than those of the terminal seven-membered rings of 7a,b. Furthermore, the average chemical shift ( $\delta_{av}$ ) of the protons on the benzene ring of **7c** ( $\delta_{av} = 8.61$ ) is lower than those of **7a** ( $\delta_{av} = 8.31$ ) and **7b** ( $\delta_{av} = 8.40$ ). Thus, the positive charge of 7c is apparently delocalized on the benzene ring as represented by the canonical structure 7cC involving the quinoid-type structure of benzene. In addition, the coupling constants of H1–H2 ( $J_{1-2} = 7.9$ Hz for **7a**,  $J_{1-2} = 8.2$  Hz for **7b**,  $J_{1-2} = 8.5$  Hz for **7c**) and H3-H4 ( $J_{3-4} = 7.7$  Hz for **7a**,  $J_{3-4} = 7.9$  Hz for **7b**,  $J_{3-4}$ = 8.4 Hz) are larger than those of H2–H3 ( $J_{2-3}$  = 7.2 Hz for **7a**,  $J_{2-3} = 7.1$  Hz for **7b**,  $J_{2-3} = 7.1$  Hz for **7c**), respectively. Thus, the C1–C2 and C3–C4 bonds have a high bond order as compared with the C2-C3 bond for 7a-c; however, the bond-length alternation of 7c appears to be larger as compared with those of 7a,b, suggesting also the important contribution of the canonical structure 7cC.

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TABLE 3.	Electronic Spectral Data of Benzocyclohepta[a]azulenylium Ions 7a-c and the Related Compounds 4, 8a,b,
and 25	

compd	solvent	$\lambda_{\rm max}/{\rm nm}~(\log\epsilon)$					
$4 \cdot BF_4^-$	CH <sub>3</sub> CN	252 (4.12), 333 (4.82), 476 (3.93), 506 (4.51), 555 (3.21), 607 (3.03), 667 (2.83), 745 (2.42)					
<b>7a</b> •BF₄ <sup>−</sup>	CH <sub>3</sub> CN	236 (4.41), 279 (4.13), 306 (4.18), 346 (4.56), 364 (4.54), 387 (4.72), 528 (4.39), 582 (3.51, sh), 635 (2.83, sh)					
<b>7b</b> •BF₄ <sup>−</sup>	CH <sub>3</sub> CN	249 (4.22), 276 (4.18), 314 (4.40), 361 (4.37), 420 (4.36), 505 (3.86, sh), 533 (4.13), 560 (3.79, sh), 614 (3.52), 670 (3.12)					
$7c \cdot BF_4^-$	CH <sub>3</sub> CN	263 (4.12), 310 (4.35), 324 (4.31), 352 (4.56, sh), 366 (4.80), 393 (4.27, sh), 497 (3.73, sh), 525 (4.13), 669 (2.90), 741 (3.00), 834 (3.03), 955 (2.79)					
8a	CH <sub>3</sub> CN CH <sub>3</sub> CN-H <sub>2</sub> SO <sub>4</sub>	250 (4.32), 289 (4.17), 349 (4.62), 399 (3.87), 422 (3.73), 587 (2.98), 641 (2.67, sh) 214 (4.71), 326 (4.38), 361 (4.57), 385 (4.74), 489 (3.86, sh), 528 (4.27)					
8b	CH <sub>3</sub> CN	238 (4.54), 272 (4.38), 287 (4.36), 301 (4.36), 335 (4.53, sh), 345 (4.58), 382 (3.91, sh), 406 (3.78), 520 (2.74, sh), 551 (2.87), 582 (2.87), 627 (2.58, sh)					
<b>25</b> •BF₄ <sup>−</sup>	CH <sub>3</sub> CN-H <sub>2</sub> SO <sub>4</sub> CH <sub>3</sub> CN	237 (4.58), 320 (4.60), 360 (4.45), 395 (4.52), 492 (3.96, sh), 516 (4.21), 558 (3.45, sh), 604 (2.63, sh) 262 (4.01), 294 (3.92), 330 (4.22), 398 (4.21, sh), 449 (4.41)					

Regarding the electronic spectra (Table 3), cations 7a-c exhibit characteristic large absorption maxima near 530 nm accompanied by slight red shifts as compared with 4 (506 nm). The corresponding absorption maximum of the cation 25, which is dihydrogenerated at the C12 and C13 positions of 7a, lies at 449 nm. The absorption is reasonably similar to that of (5-isopropyl-3,8-dimethylazulen-1-yl)phenylmethylium ion (452 nm).<sup>30</sup> Thus, the absorption maxima observed at around 530 nm are clearly due to the  $\pi$ -system bearing a benzocyclohepta[a]azulenylium skeleton. The longest absorption maxima of 7a and 7b (648 sh and 670 nm, respectively) are observed by blue shifts as compared with that of 4 (745 nm). These features suggest that the benzo-annulation onto **4** at the position having a high bond order causes enlargement of the HOMO-LUMO energy gap due to the fixation of the original  $\pi$ -conjugation by the benzene ring. On the other hand, the longest absorption maximum of 7c is observed at 955 nm, which is much shifted to longer wavelength as compared with those of **7a**,**b** and **4**. This finding is suggestive of the contribution of the canonical structures 7cA and 7cC, both of which retain a quinoidtype benzene ring, but the latter structure seemed to be more important than the former (vide supra). Actually, the electronic spectrum of 3-methoxy-2H-cyclohepta[a]azulen-2-one has been reported to exhibit the longest absorption at ca. 810 nm<sup>31</sup> due to the quinoid structure of azulene. The absorption is longer than that of 4 by 65 nm and shorter than that of 7c by 145 nm.

The spectroscopic properties of compounds 8a and 8b are interesting in relation to those of cations 7a and 7b. The <sup>1</sup>H NMR spectra and electronic spectra of **8a,b** in neutral and acidic conditions are also summarized in Table 2. The <sup>1</sup>H NMR spectra of **8a,b** in CF<sub>3</sub>CO<sub>2</sub>D shift to lower field than those in CDCl<sub>3</sub>, and proton-deuterium exchange at C11 and C13 occurs, respectively, due to the protonation onto the carbonyl oxygen as depicted in the structural formulas 29a,b (Scheme 7). The chemical shifts of protons and coupling patterns of **29a,b** are very similar to those of 7a,b, respectively, except for the protons around the carbonyl function. Furthermore, the electronic spectra of **8a,b** (**29a,b**) in CH<sub>3</sub>CN-H<sub>2</sub>SO<sub>4</sub> exhibit the characteristic large absorption at 528 and 516 nm, respectively. The spectra are very similar to those of cations 7a,b and also 4.



TABLE 4.  $pK_{R^+}$  Values and Reduction Potentials ( $E_{red}$ ) for Cyclohepta[a]azulenylium Ion Derivatives 4, 7a-c, and 25

compd	p <i>K</i> <sub>R⁺</sub> <i>a</i>	$E_{ m red}$ /V vs Ag/Ag+ $^{b}$	compd	р <i>К</i> <sub>R+</sub> а	$E_{ m red}$ /V vs Ag/Ag+ $^{+}$ $^{b}$
7 <b>a</b> ∙BF <sub>4</sub> <sup>−</sup> 7 <b>b</b> ∙BF <sub>4</sub> <sup>−</sup> 7 <b>c</b> ∙BF <sub>4</sub> <sup>−</sup>	7.3 <sup>c</sup> 5.1 <sup>c</sup> 1.6 <sup>d</sup>	-0.567 (irriv) -0.482 (irriv) -0.197 (irriv)	<b>25</b> •BF <sub>4</sub> <sup>−</sup> <b>4</b> •BF <sub>4</sub> <sup>−</sup>	4.8 <sup>c</sup> 7.3 <sup>e</sup>	-0.513 (irriv) -0.458 (irriv) <sup>f</sup>

<sup>*a*</sup> Determined spectrophotometrically at 25 °C. <sup>*b*</sup> CV peak potential in CH<sub>3</sub>CN with Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte at 0.1 V s<sup>-1</sup>. <sup>*c*</sup> In 25% aq CH<sub>3</sub>CN. <sup>*d*</sup> In 50% aq CH<sub>3</sub>CN. <sup>*e*</sup> Reference 9. <sup>*f*</sup> This work.

**Stability of Benzocyclohepta**[*a*]**azulenylium Ions 7a–c.** The affinity of the carbocations toward hydroxide ions, expressed by the  $pK_{R^+}$  value, is the most common criterion of carbocation stability.<sup>32</sup> The  $pK_{R^+}$  values of **7a–c** are determined spectrophotometrically and are summarized in Table 4, along with those of the related cations 4 and 25. The  $pK_{R^+}$  values of the cations **7a–c** are considerably affected also by benzo-annulation. The neutralization of the cation **7a,b** is completely reversible, so that immediate acidification of an alkaline solution (pH ca. 10) of **7a,b** with H<sub>2</sub>SO<sub>4</sub> regenerated the absorption maxima of the cations in the visible region to the extent of 100%. On the other hand, neutralization of the cations **7c** and **25** is not completely reversible. These features may be ascribed to the instability of the neutral-

<sup>(30)</sup> Reid, D. H.; Stafford, W. H.; Stafford, W. L.; McLennan, G.; Voigt, A. J. Chem. Soc. **1958**, 1110.

<sup>(31)</sup> Saito, M.; Morita, T.; Takase, K. Chem. Lett. 1975, 441.

<sup>(32)</sup> Freedman, H. E. *In Carbonium Ions*, Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973.



**FIGURE 3.**  $pK_{R^+}$  values against  $E_{red}$  values of **4**, **7a**-**c**, and **25**.

ized products under the conditions of the  $pK_{R^+}$  measurement. As expected, the cations **7a**,**b**, which are annulated with benzene onto the positions possessing a high bond order of **4**, are not appreciably destabilized. The  $pK_{R^+}$ value of 7a is similar to that of 4, while that of 7b is lower by 2.2 pH units than that of the parent cation 4. The relatively high destabilization effect of the cation 7b as compared with that of 7a would be attributable to the steric hindrance experienced with the hydrogens on the C1 and C13 positions to destroy the planarity of the cation. On the other hand, the cation 7c, which is benzoannulated on the positions possessing a low bond order of **4**, is destabilized remarkably; thus, the perturbation occurs on both the cyclohepta[a]azulenylium ion and the benzene ring. This feature suggests also that the positive charge of **7c** is delocalized significantly to the benzene ring, making it a quinoid-type structure. The  $pK_{R^+}$  values of 7a and 7b are larger than that of 25, which is a dihydrogenated derivative of 7a at the C12 and C13 positions, while the  $pK_{R^+}$  value of **7c** is much smaller than that of 25.

The reduction potentials ( $E_{red}$  cathodic peak potential) of 7a-c and their reference cations 25 and 4 are determined by cyclic voltammetry (CV) in CH<sub>3</sub>CN. Their waves were irreversible under the conditions of CV measurements; thus, the peak potentials are summarized in Table 4. The reduction behaviors of the cations are affected also by the position of benzo-annulation to be explained by the formation of a radical species. In Figure 3, p $K_{R^+}$  values of cations **7a**-**c** are plotted against  $E_{red}$  of these cations, as well as those of cations 4 and 25.  $E_{\rm red}$ and  $pK_{R^+}$  values have been converted to kJ mol<sup>-1</sup> [(-96.5/ kJ mol<sup>-1</sup> V<sup>-1</sup>)( $E_{red}$ /V) and (5.7/kJ mol<sup>-1</sup>)(( $pK_{R^+}$  – 14))].<sup>6,33a,b</sup> A linear correlation line was obtained for 7a-c; the slope and y-intercept of this line were 0.68 and -78.4 (correlation coefficient 0.976), respectively. The slope is smaller than 1, so it can be suggested that the more stable cations **7a**–**c** give a less stable radical species in single-electron reduction.<sup>6</sup> Thus, cations **7a**-**c** would be stabilized in a similar manner. The correlations of  $E_{\rm red}$  and  $pK_{\rm R^+}$  for **4** and **25** express deviation from the line of **7a**-**c** by 7.7 and 11.3 kJ mol<sup>-1</sup> (for **4**) and 10.1 and 14.9 kJ mol<sup>-1</sup> (for **25**), respectively. Evidently, the deviation of the plots for **4** and **25** from the slope of **7a**-**c** indicates that the cations **4** and **25** are stabilized in electronic and stereochemical situations including a neutralized species different from those of **7a**-**c**.<sup>33b,c</sup>

# Conclusion

Benzocyclohepta[*a*]azulenylium ions  $7\mathbf{a} - \mathbf{c}$ , which are annulated with benzene on the positions having a high and low bond order of cyclohepta[a]azulenylium ion (4), respectively, were synthesized for the first time. The <sup>1</sup>H NMR and electronic spectra of 7a-c suggested that the positive charges of cations 7a and 7b are localized on the terminal seven-membered rings, while that of 7c is localized on the benzo-annulated seven-membered ring. Furthermore, cation 7c has a contribution of the quinoid structure of the annulated benzene, while 7a,b do not. This feature correlates well with the stability of cations **7a**–**c**. The measurement of  $pK_{R^+}$  and reduction potentials clarified that cations 7a,b are not appreciably destabilized, while cation **7c** is much destabilized, as compared with **7a,b** as well as **4**. Furthermore, **7a,b** are more stable than 25, which has a similar skeleton but no full conjugation, while 7c is less stable than 25. Thus, it is clarified that the benzo-annulation on the low bond order of **4** giving **7c** perturbs the original  $\pi$ -system and the benzene ring to an appreciable extent. The carbonyl compounds 8a,b in acidic media exhibit spectral characteristics similar to those of cations 7a,b, respectively.

### **Experimental Section**

General experimental conditions and spectroscopic instrumentation used have been described.<sup>33</sup> The desired compounds 2H-cyclohepta[b]furan-2-one (**9**),<sup>19</sup> 5,6,8,9-tetrahydro-7*H*-benzocyclohepten-7-one (**10**),<sup>21</sup> 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (**14**),<sup>22</sup> and 5,7,8,9-tetrahydro-6*H*-benzocyclohepten-6-one (**17**)<sup>23</sup> were prepared as described in the literature.

**Preparation of 13, 16, and 20.** A solution of **10, 14**, or **17**, pyrrolidine, and TsOH·H<sub>2</sub>O in toluene or benzene was heated under reflux using a Dean–Stark apparatus. Then the solvent and the unreacted pyrrolidine were removed in vacuo to give the oil of enamine **11, 15**, or a mixture of **18** and **19**, respectively. These enamines were reacted with **9** under heating in alcoholic solutions. After evaporation of the solvent, the residue was purified through column chromatography on alumina using hexane as the eluent to give azulenoid compounds **13, 16**, and **20**, respectively. Reaction conditions and the yields of the products are also summarized in Table 1.

**Data for 12,13-dihydro-5***H***-benzocyclohepta[6,7-***a***]azulene (13): blue prisms; mp 101–102 °C (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) \delta 3.18–3.33 (2H, m), 3.40–3.53 (2H, m), 4.46 (2H, s), 6.90–7.57 (8H, m), 8.07 (1H, d, J= 9.5 Hz); 8.33 (1H, d, J= 9.5 Hz); EIMS (70 eV)** *m***/***z* **(rel intens) 244 (M<sup>+</sup>, 84), 243 (100). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>: C, 93.40; H, 6.60. Found: C, 93.22; H, 6.66.** 

**Data for 6,7-dihydro-5***H***-benzocyclohepta[6,5-***a***]azulene (16):** blue prisms; mp 129–130 °C (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  2.34 (2H, quint, J = 6.6 Hz), 2.62 (2H, t, J

<sup>(33) (</sup>a) Naya, S.; Sakakibara, T.; Nitta, M. J. Chem. Soc., Perkin Trans. 2 2001, 1032. (b) Naya, S.; Nitta, M. J. Chem. Soc., Perkin Trans. 2 2000, 2427. (c) Naya, S.; Nitta, M. J. Chem. Soc., Perkin Trans. 2 2001, 275.

= 6.6 Hz), 3.08 (2H, t, J = 6.6 Hz), 6.97–7.71 (8H, m), 8.26 (2H, d, J = 9.7 Hz); EIMS (70 eV) m/z (rel intens) 244 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>: C, 93.40; H, 6.60. Found: C, 93.17; H, 6.61.

**Data for 12,13-dihydro-5***H***-benzocyclohepta[7,6-***a***]azulene (20): blue prisms; mp 194–195 °C dec (from CH\_2Cl\_2– Et\_2O); <sup>1</sup>H NMR (90 MHz, CDCl\_3) \delta 3.37 (4H, br s), 4.45 (2H, s), 6.91–7.56 (8H, m), 8.03 (1H, d, J = 8.1 Hz), 8.10 (1H, d, J = 8.8 Hz); EIMS (70 eV)** *m/z* **(rel intens) 244 (M<sup>+</sup>, 100). Anal. Calcd for C\_{19}H\_{16}: C, 93.40; H, 6.60. Found: C, 93.44; H, 6.56.** 

General Procedure for the Oxidation of 13, 16, and 20 with DDQ. To a stirred solution of DDQ (1.135 g, 5 mmol) in aqueous acetone (50 mL, H<sub>2</sub>O-acetone, 1:9 by volume) was added a solution of 13 (489 mg, 2 mmol), 16 (489 mg, 2 mmol), or 20 (489 mg, 2 mmol) in acetone (6 mL) at 0 °C, and the mixture was stirred for another 10 min. After the acetone was evaporated, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered to remove insoluble materials. The filtrate was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the extract was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography on alumina using hexane–AcOEt (3:1) as the eluent to give 21 (476 mg, 92%), 22 (460 mg, 89%), or 23 (382 mg, 74%).

**Data for 12,13-dihydro-5***H***-cyclohepta[6,7-***a***]azulen-5one (21): red prisms; mp 144–145 °C dec (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) \delta 3.14–3.27 (2H, m), 3.37–3.50 (2H, m), 7.07 (1H, s), 7.19–7.74 (6H, m), 7.94–8.04 (1H, m), 8.27 (1H, d, J = 9.2 Hz), 9.99 (1H, d, J = 8.4 Hz); IR (CHCl<sub>3</sub>) v\_{max} 1614 cm<sup>-1</sup>; EIMS (70 eV)** *m***/***z* **(rel intens) 258 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O: C, 88.34; H, 5.46. Found: C, 88.32; H, 5.50.** 

**Data for 5,6-dihydro-***7H***-cyclohepta**[**6**,5-*a*]**azulen-7-one** (**22**): violet prisms; mp 73–74 °C (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  3.04 (4H, s), 7.34–7.92 (8H, m), 8.41 (1H, d, J = 9.5 Hz), 9.72 (1H, d, J = 8.4 Hz); IR (CHCl<sub>3</sub>)  $\nu_{max}$  1621 cm<sup>-1</sup>; EIMS (70 eV) *m/z* (rel intens) 258 (M<sup>+</sup>, 68), 229 (100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O: C, 88.34; H, 5.46. Found: C, 88.17; H, 5.46.

**Data for 5,13-dihydro-12***H***-cyclohepta[7,6-***a***]azulen-12one (23): red needles; mp 142–143 °C (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) \delta 4.17 (2H, s), 4.47 (2H, s), 7.10–7.73 (8H, m), 8.31 (1H, d, J = 9.2 Hz), 9.84 (1H, d, J = 10.1 Hz); IR (CHCl<sub>3</sub>) \nu\_{max} 1622 cm<sup>-1</sup>; EIMS (70 eV)** *m***/***z* **(rel intens) 258 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>O: C, 88.34; H, 5.46. Found: C, 88.43; H, 5.54.** 

**General Procedure for the Dehydrogeneration of 21 and 22 with DDQ.** A solution of **21** (258 mg, 1 mmol) or **22** (258 mg, 1 mmol) and DDQ (295 mg, 1.3 mmol) in 1,4-dioxane (78 mL) was heated under reflux for 5 h. After removal of the solvent, the residue was chromatographed on alumina. The fractions eluted with hexane–AcOEt (2:1) were concentrated, and the residue was purified by TLC on silica gel (hexane– AcOEt, 5:2) to give **8a** (79 mg, 47% based on consumed **21**) and unreacted **21** (88 mg, 34%) or **8b** (44 mg, 21% based on consumed **22**) and unreacted **22** (42 mg, 16%), respectively.

**Data for 5***H***-benzocyclohepta[6,7-***a***]azulen-5-one (8a):** dark purple needles; mp 112–113 °C dec (from EtOH); <sup>13</sup>C NMR (100.4 MHz, CDCl<sub>3</sub>)  $\delta$  119.4, 119.5, 125.3, 127.0, 127.6, 129.2, 129.9, 131.2, 132.7, 134.5, 135.4, 137.5, 138.8, 138.9, 139.4, 143.6, 143.7, 146.9, 186.4; IR (CHCl<sub>3</sub>)  $\nu_{max}$  1581 cm<sup>-1</sup>; EIMS (70 eV) *m*/*z* (rel intens) 256 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>12</sub>O: C, 89.04; H, 4.72. Found: C, 89.04; H, 4.58.

**Data for 7***H***-benzocyclohepta[6,5-***a***]azulen-7-one (8b):** dark violet needles; mp 129–130 °C (from EtOH); <sup>13</sup>C NMR (100.4 MHz, CDCl<sub>3</sub>)  $\delta$  117.3, 126.0, 127.8, 129.2, 129.7, 130.0, 130.5, 133.8, 134.0, 134.4, 134.5, 137.9, 138.1, 139.3, 139.9, 142.4, 142.5, 147.9, 186.8; IR (CHCl<sub>3</sub>)  $\nu_{max}$  1581 cm<sup>-1</sup>; EIMS (70 eV) *m*/*z* (rel intens) 256 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>12</sub>O: C, 89.04; H, 4.72. Found: C, 89.00; H, 4.62.

**General Procedure for the Reduction of 8a,b.** To a stirred solution of **8a** (38 mg, 0.15 mmol) or **8b** (38 mg, 0.15 mmol) and CeCl<sub>3</sub>·7H<sub>2</sub>O (67 mg, 0.18 mmol) in EtOH (2 mL) was added NaBH<sub>4</sub> (8 mg, 0.2 mmol) in EtOH (1 mL) dropwise at rt, and the mixture was stirred for another 10 min. The reaction mixture was then poured into water and extracted

with benzene, and the benzene extract was dried over  $Na_2$ -SO<sub>4</sub>. After evaporation of the benzene, the residue was chromatographed on alumina using hexane as the eluent to give **24** (36 mg, 100%) or **26** (27 mg, 75%), respectively.

**Data for 5***H***-benzocyclohepta[6,7-***a***]azulene (24): green plates; mp 152–153 °C dec (from benzene–hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) \delta 4.20 (2H, s), 7.05 (1H, dd, J = 9.8, 9.5 Hz), 7.12 (1H, d, J = 11.6 Hz), 7.17 (1H, dd, J = 9.8, 9.5 Hz), 7.20 (1H, td, J = 7.3, 1.2 Hz), 7.29–7.33 (4H, m), 7.38 (1H, d, J = 7.3 Hz), 7.49 (1H, t, J = 9.8 Hz), 8.19 (1H, d, J = 9.5 Hz), 8.45 (1H, d, J = 9.5 Hz); EIMS (70 eV) m/z (rel intens) 242 (M<sup>+</sup>, 71), 241 (100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>: C, 94.18; H, 5.82. Found: C, 94.17; H, 5.73.** 

**Data for 7***H***-benzocyclohepta[6,5-***a***]azulene (26): green prisms; mp 126–127 °C (from EtOH); <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) \delta 3.60 (2H, d, J = 6.4 Hz), 6.18 (1H, dt, J = 10.5, 6.4 Hz), 6.59 (1H, d, J = 10.5 Hz), 6.94–7.60 (7H, m), 7.88–7.99 (1H, m), 8.25 (1H, d, J = 9.5 Hz), 8.31 (1H, d, J = 9.5 Hz); EIMS (70 eV)** *m***/***z* **(rel intens) 242 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>: C, 94.18; H, 5.82. Found: C, 94.13; H, 5.78.** 

Preparation of 5H-Benzocyclohepta[6,5-a]azulene (27). To a stirred solution of **22** (101 mg, 0.39 mmol) and  $CeCl_3$ · 7H<sub>2</sub>O (223 mg, 0.60 mmol) in EtOH (15 mL) was added a solution of NaBH<sub>4</sub> (42 mg, 1.1 mmol) in EtOH (2 mL), and the mixture was stirred at rt for 5 min. The reaction mixture was poured into water and extracted with benzene, and the benzene extract was dried over Na<sub>2</sub>SO<sub>4</sub>. After the benzene was removed, the residue and TsCl (384 mg, 2.0 mmol) were dissolved in pyridine (8 mL), and the mixture was stirred at rt for 39 h. To this reaction mixture was added saturated aqueous CuSO<sub>4</sub> solution, the mixture was extracted with benzene, and the extract was dried over MgSO<sub>4</sub>. After evaporation of the benzene, the residue was purified by TLC on alumina (hexane-AcOEt, 20:1) to give 27 (69 mg, 73%) as green prisms: mp 173-174 °C (from EtOH); <sup>1</sup>H NMR (90 MHz,  $CDCl_3$ )  $\delta$  3.20 (2H, d, J = 6.8 Hz), 6.16 (1H, dt, J = 9.9, 6.8 Hz), 7.03-7.89 (9H, m), 8.34 (1H, d, J = 9.5 Hz), 8.40 (1H, d, J = 9.2 Hz); EIMS (70 eV) m/z (rel intens) 242 (M<sup>+</sup>, 90), 149 (100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>: C, 94.18; H, 5.82. Found: C, 93.85; H, 5.75.

Preparation of 5*H*-Benzocyclohepta[7,6-*a*]azulene (28). To a stirred solution of 23 (101 mg, 0.39 mmol) and  $CeCl_3$ . 7H<sub>2</sub>O (177 mg, 0.48 mmol) in THF-EtOH (4 mL, 1:1 by volume) was added NaBH<sub>4</sub> (17 mg, 0.45 mmol) in EtOH (1 mL) dropwise, and the mixture was stirred at rt for 1 h. The reaction mixture was poured into water and extracted with benzene, and the benzene extract was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the benzene gave crystals of alcohol, which were dissolved in benzene (20 mL) containing TsOH·H<sub>2</sub>O (10 mg), and the mixture was stirred at rt for 15 min. The reaction mixture was then chromatographed on alumina using benzene as the eluent to give 28 (76 mg, 80%) as green needles: mp 191-193 °C dec (from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O); <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ )  $\delta$  4.16 (2H, s), 6.95 (1H, d, J = 11.6 Hz), 7.11 (1H, dd, J = 9.7, 9.5 Hz), 7.15–7.19 (1H, m), 7.19 (1H, dd, J = 7.6, 7.3Hz), 7.23 (1H, s), 7.25 (1H, dd, J = 7.6, 7.3 Hz), 7.30 (1H, d, J = 7.6 Hz), 7.32 (1H, d, J = 7.6 Hz), 7.50 (1H, d, J = 11.6 Hz), 7.53 (1H, dd, J = 9.7, 9.0 Hz), 8.22 (1H, d, J = 9.5 Hz), 8.35 (1H, d, J = 9.5 Hz); EIMS (70 eV) m/z (rel intens) 242 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>: C, 94.18; H, 5.82. Found: C, 94.24; H, 5.79.

General Procedure for the Preparation of  $7a \cdot BF_4^-$ , 7b·BF<sub>4</sub><sup>-</sup>, and 7c·BF<sub>4</sub><sup>-</sup>. A solution of 24 (24.2 mg, 0.1 mmol), 26 (24.2 mg, 0.1 mmol), or 28 (24.2 mg, 0.1 mmol) and TrBF<sub>4</sub> (39.6 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was stirred at rt for 5–30 min. To the reaction mixture was added Et<sub>2</sub>O, and the precipitates were filtered and washed with Et<sub>2</sub>O to give the salt  $7a \cdot BF_4^-$  (28.2 mg, 86%),  $7b \cdot BF_4^-$  (21.2 mg, 65%), or  $7c \cdot BF_4^-$  (27.3 mg, 83%).

**Data for benzocyclohepta**[6,7-*a*]**azulenylium tetrafluoroborate (7a·BF**<sub>4</sub><sup>-</sup>): brown needles; mp 222–223 °C dec (from CH<sub>3</sub>CN); <sup>13</sup>C NMR (100.4 MHz, CD<sub>3</sub>CN)  $\delta$  121.9, 128.7,

130.6, 132.8, 134.5, 136.5, 136.7, 137.4, 139.0, 139.8, 140.5, 140.6, 142.2, 142.3, 142.5, 146.3, 149.6, 153.5, 158.1; IR (KBr)  $\nu_{\rm max}$  1395, 1084 cm $^{-1}$ . Anal. Calcd for C $_{19}H_{13}BF_4$ : C, 69.55; H, 3.99. Found: C, 69.40; H, 4.23.

**Data for benzocyclohepta**[6,5-*a*]**azulenylium tetrafluoroborate (7b·BF**<sub>4</sub><sup>-</sup>): brown powder; mp 115–117 °C dec (from CH<sub>3</sub>CN–AcOEt); <sup>13</sup>C NMR (125.8 MHz, CD<sub>3</sub>CN)  $\delta$  124.8. 127.2, 130.3, 132.8, 133.6, 134.7, 135.9, 137.5, 138.4, 138.8, 139.6, 140.7, 141.1, 143.6, 145.2, 146.2, 151.8, 152.7, 154.3; IR (KBr)  $\nu_{max}$  1390, 1084 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>13</sub>BF<sub>4</sub>: C, 69.55; H, 3.99. Found: C, 69.59; H, 3.90.

**Data for benzocyclohepta**[**7,6**-*a*]**azulenylium tetrafluoroborate (7c·BF**<sub>4</sub><sup>-</sup>): brown needles; mp > 300 °C (from CF<sub>3</sub>-CO<sub>2</sub>H-CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O); <sup>13</sup>C NMR (125.8 MHz, CF<sub>3</sub>CO<sub>2</sub>D)  $\delta$  124.5, 132.5, 134.1, 134.3, 134.7, 137.3, 138.7, 139.2, 140.3, 142.8, 143.3, 144.5, 145.6, 146.5, 146.9, 149.1, 149.2, 149.3, 155.6; IR (KBr)  $\nu_{max}$  1384, 1084 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>13</sub>-BF<sub>4</sub>: C, 69.55; H, 3.99. Found: C, 69.71; H, 3.94.

Alternative Preparation of 7b·BF<sub>4</sub><sup>-</sup>. A solution of 27 (24.2 mg, 0.1 mmol) and TrBF<sub>4</sub> (53 mg, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was stirred at rt for 27 h. After addition of Et<sub>2</sub>O to the reaction mixture, the precipitates were collected by filtration and washed with Et<sub>2</sub>O to give 7b·BF<sub>4</sub><sup>-</sup> (31.4 mg, 96%), which was identical with the authentic specimen.

**General Procedure for the Reduction of 7a–c·BF**<sub>4</sub><sup>-</sup>. A solution of **7a**·BF<sub>4</sub><sup>-</sup> (16.4 mg, 0.05 mmol), **7b**·BF<sub>4</sub><sup>-</sup> (16.4 mg, 0.05 mmol), or **7c**·BF<sub>4</sub><sup>-</sup> (16.4 mg, 0.05 mmol) and NaBH<sub>4</sub> (2.7 mg, 0.07 mmol) in CH<sub>3</sub>CN (2 mL) was stirred at rt for 10 min. The reaction mixture was poured into water and extracted with benzene, and the benzene extract was dried over Na<sub>2</sub>-SO<sub>4</sub>. After evaporation of the benzene, the residue was purified by TLC on alumina (hexane–benzene, 7:2) to give **25** (12.1 mg, 100%), a mixture of **26** (10.7 mg, 88%) and **27** (0.5 mg, 4%), or **28** (5.7 mg, 47%), respectively.

**Preparation of 12,13-Dihydrobenzocyclohepta[6,7-a]azulenylium Tetrafluoroborate (25·BF**<sub>4</sub><sup>-</sup>). A solution of **13** (82 mg, 0.34 mmol) and TrBF<sub>4</sub> (122 mg, 0.37 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was stirred at rt for 1 h. To this reaction mixture was added Et<sub>2</sub>O, and the precipitate was collected by filtration and washed with Et<sub>2</sub>O to give **25·**BF<sub>4</sub><sup>-</sup> (101 mg, 91%) as red needles: mp 155–156 °C dec (from CH<sub>3</sub>CN-Et<sub>2</sub>O); <sup>13</sup>C NMR(100.4 MHz, CD<sub>3</sub>CN) δ 29.6, 33.1, 129.1, 131.9, 132.6, 134.6, 136.6, 138.5, 139.2, 139.6, 142.6, 144.3, 145.9, 146.9, 147.1, 151.8, 156.4, 161.6, 162.6; IR (KBr)  $\nu_{max}$  1444, 1084 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>15</sub>BF<sub>4</sub>: C, 69.13; H, 4.58. Found: C, 68.98; H, 4.50.

**Reduction of 25·BF**<sub>4</sub><sup>-</sup>. A solution of **25·B**F<sub>4</sub><sup>-</sup> (18 mg, 0.055 mmol) and NaBH<sub>4</sub> (4.0 mg, 0.10 mmol) in CH<sub>3</sub>CN (2 mL) was stirred at rt for 5 min. To this reaction mixture was added water, the mixture was extracted with Et<sub>2</sub>O, and the Et<sub>2</sub>O extract was dried over MgSO<sub>4</sub>. Evaporation of the solvent afforded **13** (13 mg, 100%), which was identical with the authentic specimen.

Determination of pK<sub>R<sup>+</sup></sub> Values for Benzocyclohepta-[a]azulenylium Tetrafluoroborates 7a-c·BF<sub>4</sub>- and the **Related Compound 25.BF**<sub>4</sub><sup>-</sup>. Buffer solutions of slightly different acidities of pH 10-8 were prepared by various proportions of B(OH)3-KCl-NaOH in CH3CN/H2O (1:3 by volume). Buffer solutions of pH 8-2 were prepared by various proportions of citric acid-Na<sub>2</sub>HPO<sub>4</sub> in CH<sub>3</sub>CN/H<sub>2</sub>O (1:3 by volume). Buffer solutions of pH 2–1 were prepared by various proportions of HCl-KCl in ĈH<sub>3</sub>CN/H<sub>2</sub>O (1:1 by volume). The sample solutions with higher acidity were made by further addition of 1-3 drops of  $H_2SO_4$ . The concentration of the cations was 0.05  $\hat{mmol}$  L<sup>-1</sup>. The electronic spectra were recorded by using a 1 cm cell at 25 °C on each cation in 15 solutions of buffers spaced through a pH range of about two units on each side of the  $pK_{R^+}$ . Immediately after the spectrum was recorded, the pH of each sample solution was determined on a pH meter calibrated with standard buffers before use. After complete neutralization of each cation, confirmation of the reversibility was carried out by qualitative regeneration of the cation spectrum upon acidification of the solution with H<sub>2</sub>SO<sub>4</sub>. The reversibility of the cations **7a,b** was confirmed, but slight decomposition of the cations 7c and 25 was observed. The  $pK_{R^+}$  values obtained are listed in Table 4.

Cyclic Voltammetry of Benzocyclohepta[a]azulenylium Tetrafluoroborates 7a-c·BF4- and the Related **Compounds**  $4 \cdot BF_4^-$  **and**  $25 \cdot BF_4^-$ **.** Reduction potentials of the salts  $7a \cdot BF_4^-$ ,  $7b \cdot BF_4^-$ ,  $7c \cdot BF_4^-$ ,  $4 \cdot BF_4^-$ , and  $25 \cdot BF_4^-$  were determined by means of a voltammetry controller. A threeelectrode cell was used, consisting of Pt working and counter electrodes and a reference electrode, Ag/AgNO<sub>3</sub>. A CH<sub>3</sub>CN solution (4 mL) of the salts (1 mmol  $L^{-1}$ ) and  $Bu_4NClO_4$  (100 mmol L<sup>-1</sup>) was deaerated by bubbling nitrogen through the solution. The measurements were made at a scan rate of 0.1 V s<sup>-1</sup>, and the voltammograms were recorded on an X-Yrecorder. Immediately after the measurements, ferrocene (0.2 mmol L<sup>-1</sup>) ( $E_{1/2}$  = +0.083 V) was added as an internal standard, and the observed cathodic peak potential was corrected with reference to this standard. All the cations showed common irreversible reduction waves. The cathodic peak potentials, *E*<sub>red</sub>, are summarized in Table 4.

**Acknowledgment.** We thank the Materials Characterization Central Laboratory, Waseda University, for technical assistance with the spectral data and elemental analyses.

**Supporting Information Available:** <sup>1</sup>H NMR, <sup>13</sup>C NMR, and electronic spectra for  $4 \cdot BF_4^-$ ,  $7a - c \cdot BF_4^-$ , **8a,b**, and  $25 \cdot BF_4^-$  and <sup>1</sup>H-<sup>1</sup>H COSY spectra of  $7a - c \cdot BF_4^-$  and **8a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020136A