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Synthesis, Properties, and Oxidizing Ability of Areno-Annulated 1,3-Dimethyl-10-phenylcyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1,3*H*)-dionylium Ions

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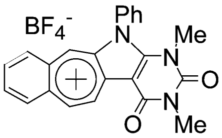

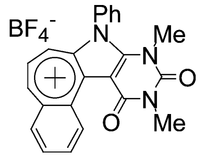

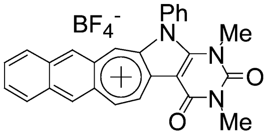

Novel areno-annulated 1,3-dimethyl-10-phenylcyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1,3*H*)-dionylium ions $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ and $\mathbf{16a^{+}\cdot BF_4^{-}}$ were synthesized by three-step reactions, starting from the reactions of benzo[*b*]tropone and naphtho[2,3-*d*]tropone with 6-anilino-1,3-dimethyluracil. Structural characteristics of $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ were clarified on inspection of the UV−vis and NMR spectral data as well as by X-ray crystal analyses. The stability of cations $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ is expressed by the pK_{R+} values which were determined spectrophotometrically as the values of ca. 0.5−9.0. The pK_{R+} value of the naphtho[*b*]tropylium ion $\mathbf{4}^{+}$ was clarified to be much lower, at <0. The electrochemical reduction of $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ exhibited reduction potentials at −0.46 to −0.67 (V vs Ag/$AgNO_3$) upon cyclic voltammetry (CV). The reduction potentials of the benzotropylium ion and cation $\mathbf{4}^{+}$ were −0.26 and −0.09 V, respectively. In a search for reactivity, reactions of $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ with some nucleophiles, hydride and diethylamine, were carried out. Although the reactions of $\mathbf{12a^{+}\cdot BF_4^{-}}$ afforded C11 adduct **19** as a single product, the addition reactions of $\mathbf{12b^{+}\cdot BF_4^{-}}$ proceeded at both C9 and C11. The attempted reduction of methyl benzoylformate by using **21** was carried out unsuccessfully. The photoinduced oxidation reaction of $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ and $\mathbf{16a^{+}\cdot BF_4^{-}}$ toward some amines under aerobic conditions was carried out to give the corresponding imines (isolated by converting to the corresponding 2,4-dinitrophenylhydrazones) with the recycling number of 3.6−21.7.

Introduction

The concept of aromaticity is fundamental to rationalize and understand the structure and reactivity of many known chemical species.[1] In the quest for a better understanding of this concept, the study of compounds with condensed benzene rings has occupied many organic and theoretical chemists. Polyacenes are polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings. These long-known substances have attracted the wide interest of both theoretical and experimental scientists.[2] Among these substances, pentacene has received much attention as an active semiconducting material in field-effect transistors because of its unusually high charge-carrier mobility.[3] On the other hand, helicenes have also attracted general interest because of their repeating structural motif of ortho-fused aromatic rings

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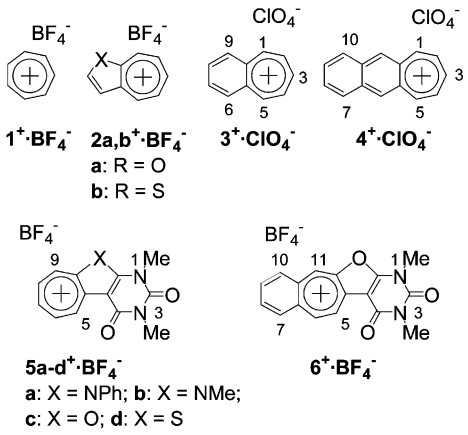
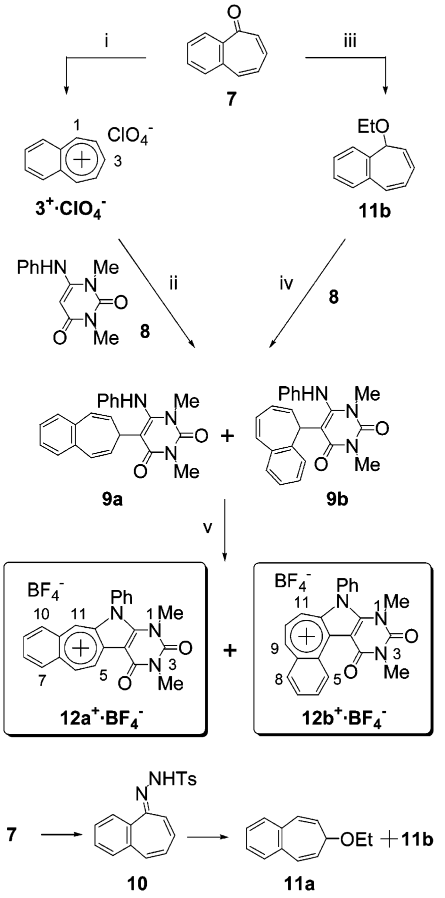


FIGURE 1. Annulated tropylium ions.

that result in a unique combination of the following features: helical chirality, inherently strong chromophores, and the possibility for steric/electronic interactions between overlapping rings.[4] Thus, the π-conjugation mode in polycyclic conjugated π-systems containing more than one $(4n + 2)$ conjugation loop is an important subject from both theoretical and experimental viewpoints. The combination of more than one π-system can endow the original π-system with new properties. Previously, we have studied the synthesis and structural and chemical properties of catacondensed aromatic π-systems, azuleno[1,2-*a*]azulene derivatives[5] and azuleno-annulated 1,6-methano[10]-annulene derivatives.[6] We have now focused our attention on the cycloheptatrienylium (tropylium) ion $\mathbf{1^+\cdot BF_4^-}$ (Figure 1), which has fair thermodynamic stability (pK_{R+} = 3.9).[7] Although the tropylium ion $\mathbf{1}^+$ is stabilized by annulation with five-membered aromatic heterocycles, as demonstrated by cations $\mathbf{2a}^+$ and $\mathbf{2b}^+$ ($\mathbf{2a}^+$ pK_{R+} = 6.7; $\mathbf{2b}^+$ pK_{R+} = 6.0),[8,9] tropylium ions annulated with benzene, $\mathbf{3}^+$, have been appreciably destabilized (pK_{R+} = 1.6).[10] In addition, because the synthesis of naphtho-annulated tropylium ion $\mathbf{4}^+$ has been reported,[11] its stability and electrochemical properties are also interesting.

SCHEME 1[a]



[a] Reagents and conditions: (i) (a) $LiAlH_4$, Et_2O, room temperature, 0.5 h; (b) 60% aqueous $HClO_4$, Ac_2O, 0 °C, 20 min; (ii) NaH, CH_3CN, −40 °C, 20 h; (iii) $NaBH_4$, $CeCl_3$, molecular sieve of 0.4 nm, EtOH, reflux, 4 h; (iv) *p*-TsOH, molecular sieve of 0.4 nm, CH_3CN, room temperature, 6 h; (v) (a) DDQ, $CHCl_3$, reflux, 16 h; (b) 42% aqueous HBF_4, Ac_2O, 0 °C, 1 h.

On the other hand, we have reported the synthesis, properties, and reactivity of 1,3-dimethylcyclohepta[4,5]pyrrolo[2,3-*d*]-pyrimidine-2,4(1,3*H*)-dionylium ion $\mathbf{5a,b^+\cdot BF_4^-}$[12] and its furan and thiophene analogues $\mathbf{5c^+\cdot BF_4^-}$[13] and $\mathbf{5d^+\cdot BF_4^-}$[14] as well as their novel photoinduced autorecycling oxidizing reactions toward some alcohols and amines.[15] In this context, we have recently reported the synthesis, properties, and oxidizing ability of $\mathbf{6^+\cdot BF_4^-}$.[16] The properties and reactivity of compound $\mathbf{6^+\cdot BF_4^-}$ were much perturbed by the benzo annulation on $\mathbf{5c^+\cdot BF_4^-}$. Thus, the areno annulation onto $\mathbf{5a^+\cdot BF_4^-}$ is a very interesting project from the viewpoint of exploration of novel functions. In this study, we have investigated the synthesis of novel cations $\mathbf{12a,b^+\cdot BF_4^-}$ (Scheme 1) and $\mathbf{16a^+\cdot BF_4^-}$ (Scheme 2), which are derived from annulation of $\mathbf{5a}^+$ with benzene and naphthalene rings. Their structural characteristics were deduced on the basis of the UV−vis and NMR spectral data as well as by X-ray crystal analyses. The stability and electrochemical properties of $\mathbf{12a,b^+\cdot BF_4^-}$ and $\mathbf{16a^+\cdot BF_4^-}$ as well as those of naphtho[*b*]tropylium ion $\mathbf{4^+\cdot ClO_4^-}$ were demonstrated. In a search for reactivity, reactions of $\mathbf{12a,b^+\cdot BF_4^-}$ with some nucleophiles, hydride and diethylamine, were carried out. The photoinduced oxidizing reaction of $\mathbf{12a,b^+\cdot BF_4^-}$ and $\mathbf{16a^+\cdot BF_4^-}$

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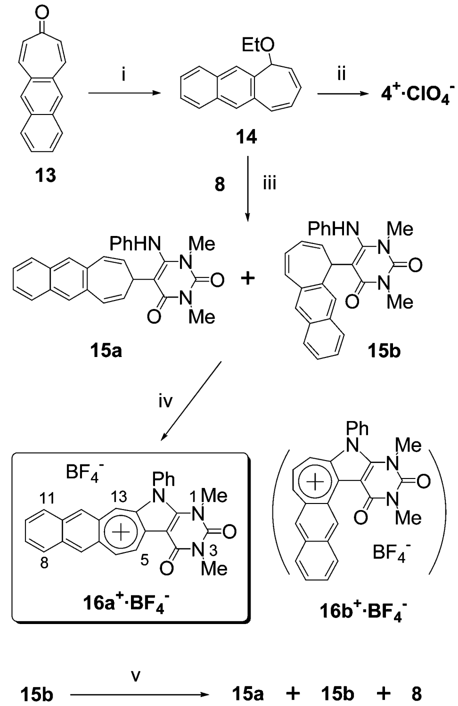
SCHEME 2 [a]



[a] Reagents and conditions: (i) $NaBH_4$, $CeCl_3$, molecular sieve of 0.4 nm, EtOH, reflux, 5 h; (ii) 60% aqueous $HClO_4$, Ac_2O, 0 °C, 20 min; (iii) *p*-TsOH, molecular sieve of 0.4 nm, CH_3CN, room temperature, 3 h; (iv) (a) $CHCl_3$, reflux, 6 h; (b) DDQ, $CHCl_3$, reflux, 16 h; (b) 42% aqueous HBF_4, Ac_2O, 0 °C, 1 h; (v) $CHCl_3$, CD_3CN, 60 °C, 6 h.

toward some amines was investigated as well. We report here the results in detail.

Results and Discussion

Synthesis. The synthesis of $\mathbf{12a^+{\cdot}BF_4^-}$ and $\mathbf{12b^+{\cdot}BF_4^-}$ was accomplished by three-step reactions starting from benzo[*b*]tropone **7** (Scheme 1). According to the reported procedure,[17] the benzotropylium cation $\mathbf{3^+{\cdot}ClO_4^-}$ was prepared by the reduction of benzo[*b*]tropone **7**[18] with $LiAlH_4$ and subsequent dehydroxylation by $HClO_4$. A reaction of $\mathbf{3^+{\cdot}ClO_4^-}$ with 1,3-dimethyl-6-phenylaminouracil **8** in CH_3CN in the presence of NaH at −40 °C for 20 h gave a mixture of **9a** and **9b** in a good combined yield (82%). The ratio of **9a** and **9b** was determined to be 1:5 from the ^1H NMR spectrum of the mixture. Because the cation $\mathbf{3^+{\cdot}BF_4^-}$ is unstable ($pK_{R+} = 1.6$),[10] the stray water in the solvent causes lowering of the yield of **9a,b**. Consequently, an alternative route via 5-ethoxy-5*H*-benzocycloheptene **11b** was studied. Previously, the synthesis of **11b** from **7** via hydrazone **10** has been reported;[19] however, the yield of **10** was modest (50%) and the reaction of **10** afforded a mixture of **11a** and **11b**. Thus, as the modified procedure, the one-step reduction of **7** with $NaBH_4$ in EtOH in the presence of $CeCl_3$ and molecular sieves (0.4 nm) was carried out to give **11b** in 94% yield. It is noteworthy that **11b** was a single product, and no generation of **11a** was observed. The result is probably due to the more stable nature of **11b**, suggested by the calculated heat of formation (vide infra). A reaction of **8** with **11b** in CH_3CN in the presence of *p*-TsOH at room temperature for 6 h afforded a mixture of **9a** and **9b** in almost quantitative yield (99%). The ratio of **9a** and **9b** was determined to be 1:5 from the ^1H NMR spectrum of the mixture. Thus, the synthesis of desired compounds **9a,b** was achieved without isolation of unstable cation $\mathbf{3}^+$. Because compounds **9a,b** were unstable on SiO_2 and Al_2O_3, these regioisomers could not be separated, and thus, the mixture of **9a** and **9b** was used for further reaction. A heating of the mixture of **9a** and **9b** with DDQ in $CHCl_3$ under reflux for 16 h and a subsequent anion exchange reaction using aqueous HBF_4 in Ac_2O afforded a mixture of $\mathbf{12a^+{\cdot}BF_4^-}$ and $\mathbf{12b^+{\cdot}BF_4^-}$ in a moderate yield. Separation of $\mathbf{12a^+{\cdot}BF_4^-}$ and $\mathbf{12b^+{\cdot}BF_4^-}$ was accomplished by fractional recrystallization from CH_3CN/AcOEt to give pure samples of $\mathbf{12a^+{\cdot}BF_4^-}$ and $\mathbf{12b^+{\cdot}BF_4^-}$. Although the ratio of starting **9a** and **9b** was 1:5, the yields of products $\mathbf{12a^+{\cdot}BF_4^-}$ and $\mathbf{12b^+{\cdot}BF_4^-}$ were 30% and 8%, respectively. This fact suggests that the rearrangement from **9b** to **9a** would occur under the reaction conditions (vide infra).

The synthesis of naphtho-annulated derivative $\mathbf{16a^+{\cdot}BF_4^-}$ was accomplished by a similar route starting from naphtho[2,3-*d*]tropone **13**[20] (Scheme 2). The reduction of **13** with $NaBH_4$ in EtOH in the presence of $CeCl_3$ and molecular sieves (0.4 nm) was carried out to give **14** in 95% yield as a single product. In addition, the treatment of **14** with 70% aqueous $HClO_4$ in Ac_2O afforded naphtho[*b*]tropylium ion $\mathbf{4^+{\cdot}ClO_4^-}$ in 64% yield. Thus, the reduction of tropone derivatives using $NaBH_4$ in the presence of $CeCl_3$ would provide a useful method for the generation of unstable tropylium ions. The reaction of **8** with **14** in CH_3CN in the presence of *p*-TsOH at room temperature for 3 h afforded a mixture of **15a** and **15b** in almost quantitative yield (99%). The ratio of **15a** and **15b** was determined to be 1:7 from the ^1H NMR spectrum of the mixture. Heating of the mixture of **15a,b** and DDQ in $CHCl_3$ under reflux for 16 h and a subsequent anion exchange reaction using aqueous HBF_4 in Ac_2O afforded $\mathbf{16a^+{\cdot}BF_4^-}$, which is expected from **15a**, in a modest yield (19%) as a single product, and generation of $\mathbf{16b}^+$ was not observed. Apparently, rearrangement from **15b** to **15a** would occur under the reaction conditions. Because **15b** could be isolated by recrystallization of a mixture of **15a** and **15b**, thermal reactions of **15b** in the absence or presence of $CHCl_3$ were monitored by ^1H NMR spectroscopy in acid-free $CDCl_3$ prepared by passing through basic Al_2O_3. By heating at 60 °C for 6 h, the reaction of **15b** in the absence of $CHCl_3$ afforded a mixture of **8**, **15a**, and **15b** in a ratio of 0.01:0.04:1.00. In contrast, the reaction in the presence of $CHCl_3$ afforded a mixture of **8**, **15a**, and **15b** in a ratio of 0.03:1.40:1.00, suggesting that the acid-catalyzed rearrangement from **15b** to **15a** and decomposition would occur. Consequently, the method for synthesizing $\mathbf{16a^+{\cdot}BF_4^-}$ was modified as follows: A solution of **15a** and **15b** in $CHCl_3$ was heated at 60 °C for 6 h, followed by addition of DDQ. The resulted mixture was heated under reflux for 16 h, and a subsequent anion exchange reaction using aqueous HBF_4 in Ac_2O afforded $\mathbf{16a^+{\cdot}BF_4^-}$ in a better yield (25%). To clarify the product ratios in the reduction of **7** and **13** as well as in the substitution reaction of **11b** and **14**, MO calculations of **9a,b** and **15a,b** as well as of MeO-substituted model compounds **17a,b** and **18a,b** were carried out using the AM1 method (MOPAC97),[21] and their heat of formation is summarized in Figure 2. Compounds **17a** and **18a** are less stable

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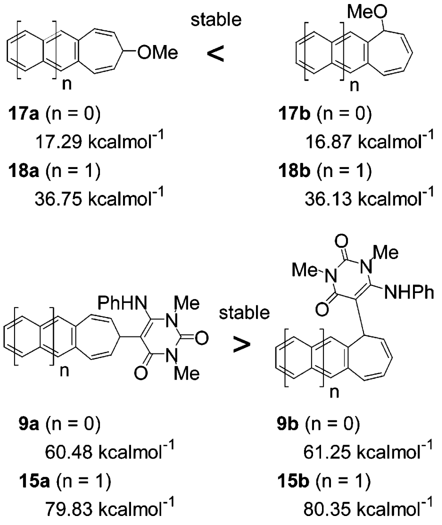

FIGURE 2. Calculated heat of formation (kcal/mol).

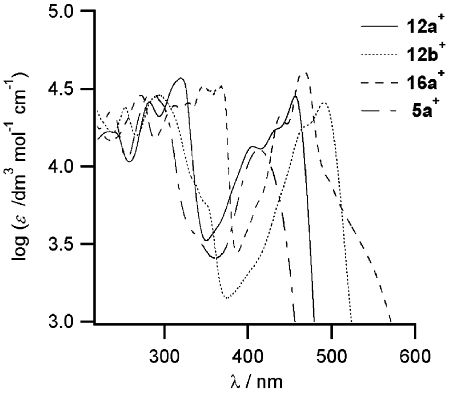

FIGURE 3. UV−vis spectra of $\mathbf{5a^+{\cdot}BF_4^-}$, $\mathbf{12a,b^+{\cdot}BF_4^-}$, and $\mathbf{16a^+{\cdot}BF_4^-}$ in CH_3CN.

than **17b** and **18b**, respectively. In addition, the acid-catalyzed rearrangement from **17a** to **17b** has been reported.[22] Thus, exclusive generation of **11b** and **14** would be rationalized from the thermodynamic stability and possible rearrangement in the presence of $CeCl_3$ under thermal conditions. In contrast, the reactions of **11b** and **14** with **8** proceeded under relatively low temperature, and thus, the reactions seem to proceed kinetically. Concerning uracil adducts **9a,b** and **15a,b**, compounds **9a** and **15a** are more stable than **9b** and **15b**, respectively, and thus, the rearrangement from **9b** to **9a** as well as that from **15b** to **15a** would proceed under acidic and thermal conditions.

Properties. Compounds $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ were fully characterized on the basis of the ^{1}H NMR, ^{13}C NMR, IR, UV−vis, and mass spectral data, as well as by elemental analyses and X-ray analyses. Mass spectra of $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ exhibited the correct $M^+-BF_4^-$ ion peak, which is indicative of the cationic nature of the compound. The characteristic absorption band for the counterion BF_4^- was observed at 1084 cm^{-1} in the IR spectra. UV−vis spectra of $\mathbf{12a,b^+}$ and $\mathbf{16a^+}$ in acetonitrile are shown in Figure 3, together with that of $\mathbf{5a^+}$. The longest wavelength absorption maxima (λ_{max}) become longer in the order $\mathbf{5a^+} < \mathbf{12a^+} < \mathbf{16a^+}$, suggesting the elongated π-conjugation (Table 1). In addition, λ_{max} of $\mathbf{12b^+}$ shows a large red-shift by 77 and 34 nm, as compared with those of $\mathbf{5a^+}$ and $\mathbf{12a^+}$, respectively. The feature would be explained by considering the raised HOMO of $\mathbf{12b^+}$ due to the large deformation of the π-system from planarity (vide infra).

TABLE 1. λ_{max}, pK_{R+} Values, and Reduction Potentials[a] of Cations $\mathbf{2^+}$, $\mathbf{3^+}$, $\mathbf{12a,b^+}$, and $\mathbf{16a,b^{+}}$[b] and Reference Compounds $\mathbf{1^+}$ and $\mathbf{5a^+}$

compd	λ_{max}/nm	pK_{R+}	reduction potential ($E1_{red}$/V)
$\mathbf{12a^+}$	457	9.0	−0.67
$\mathbf{12b^+}$	491	ca. 0.5	−0.49
$\mathbf{16a^+}$	467	6.3	−0.46
$\mathbf{1^+}$ [c]	273	3.9	−0.51
$\mathbf{3^+}$ [d]	426	1.6	−0.26
$\mathbf{4^+}$ [e]	593	< 0	−0.09
$\mathbf{5a^+}$ [f]	414	10.9	−0.84

[a] V vs Ag/AgNO$_3$: cathodic peak potential. [b] Salts $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ as well as salts $\mathbf{3^+{\cdot}ClO_4^-}$ and $\mathbf{4^+{\cdot}ClO_4^-}$ were used for the measurement. [c] Ref 7. [d] Ref 10. [e] Ref 11. [f] Ref 12.

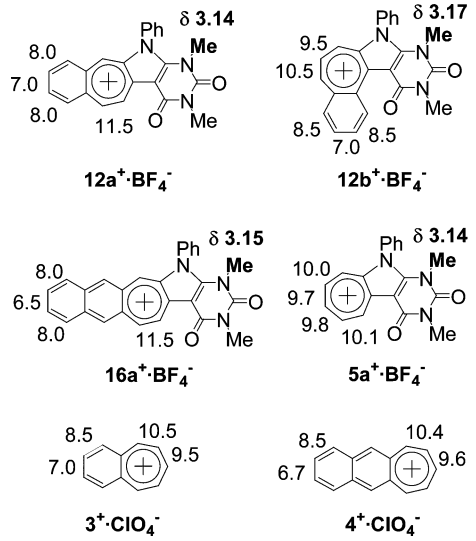

FIGURE 4. Chemical shifts and coupling constants of $\mathbf{12a,b^+{\cdot}BF_4^-}$, $\mathbf{16a^+{\cdot}BF_4^-}$, $\mathbf{5a^+{\cdot}BF_4^-}$, $\mathbf{3^+{\cdot}ClO_4^-}$, and $\mathbf{4^+{\cdot}ClO_4^-}$.

The ^{1}H NMR spectra of $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ are noteworthy because the chemical shifts of fused aromatic ring systems are quite useful in determining structural properties such as diatropicity and bond alternation. Unambiguous proton assignments were made by analyzing ^{1}H NMR, H−H COSY, and NOE spectra. The chemical shift of N1Me and selected coupling constants of the peripheral protons of $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ are shown in Figure 4, together with those of the reference compounds $\mathbf{3^+{\cdot}ClO_4^-}$,[10] $\mathbf{4^+{\cdot}ClO_4^-}$,[11] and $\mathbf{5a^+{\cdot}BF_4^-}$.[12] The corrected and precise proton assignment of $\mathbf{4^+{\cdot}ClO_4^-}$ was made by analyzing ^{1}H NMR and H−H COSY spectra in this study. The proton signal of N1Me of $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ ($\mathbf{12a^+{\cdot}BF_4^-}$, δ 3.14; $\mathbf{12b^+{\cdot}BF_4^-}$, δ 3.17; $\mathbf{16a^+{\cdot}BF_4^-}$, δ 3.15) is remarkably shifted to a higher field as compared with that of N1Me of $\mathbf{5b^+{\cdot}BF_4^-}$ (δ 3.94),[12] suggesting that N1Me of $\mathbf{12a,b^+{\cdot}BF_4^-}$ and $\mathbf{16a^+{\cdot}BF_4^-}$ is located within the shielding region of the phenyl group. This feature is similar to that of $\mathbf{5a^+{\cdot}BF_4^-}$ and is confirmed by X-ray structure analysis (vide infra). Concerning the seven-membered ring, $\mathbf{12a^+{\cdot}BF_4^-}$ [$J_{5,6} = 11.5$ Hz], $\mathbf{12b^+{\cdot}BF_4^-}$ [$J_{9,10} = 10.5$ Hz, $J_{10,11} = 9.5$ Hz],

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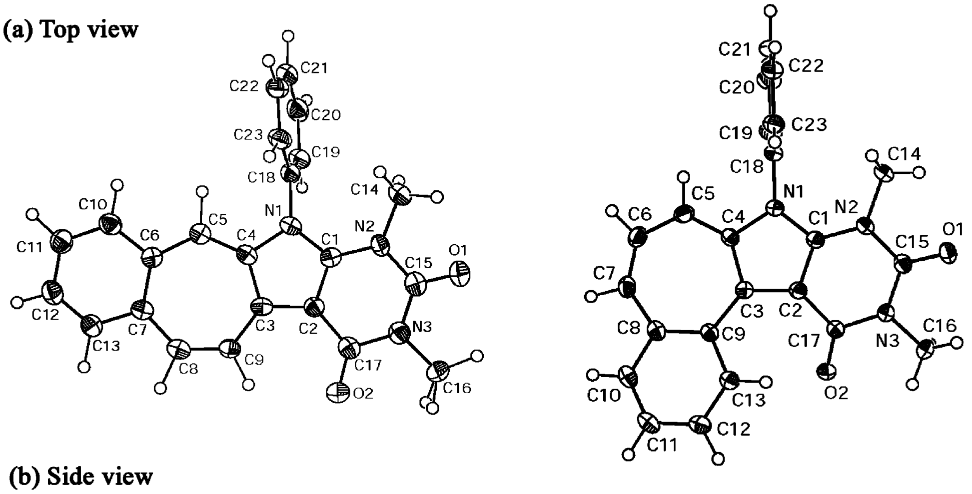
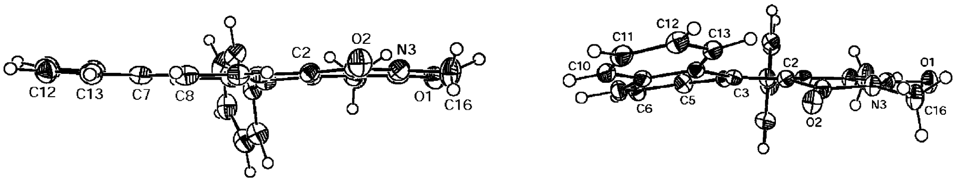
(a) Top view



(b) Side view



$\mathbf{12a}^{+}$ $\mathbf{12b}^{+}$

FIGURE 5. ORTEP drawings of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ with a thermal ellipsoid plot (50% probability). Selected bond lengths (Å) of $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$: N1−C1, 1.355; N1−C4, 1.414; C1−C2, 1.395; C2−C3, 1.393; C3−C4, 1.441; C4−C5, 1.365; C5−C6, 1.421; C6−C7, 1.425; C7−C8, 1.439; C8−C9, 1.353; C3−C9, 1.417; C6−C10, 1.427; C10−C11, 1.360; C11−C12, 1.404; C12−C13, 1.369; C7−C13, 1.415. Selected bond lengths (Å) of $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$: N1−C1, 1.354; N1−C4, 1.411; C1−C2, 1.417; C2−C3, 1.416; C3−C4, 1.442; C4−C5, 1.374; C5−C6, 1.403; C6−C7, 1.363; C7−C8, 1.431; C8−C9, 1.442; C3−C9, 1.450; C8−C10, 1.429; C10−C11, 1.365; C11−C12, 1.409; C12−C13, 1.378; C9−C13, 1.414.

and $\mathbf{16a}^{+}\cdot\mathbf{BF_4}^{-}$ [$J_{5,6} = 11.5$ Hz] show larger bond alternations as compared with that of $\mathbf{5a}^{+}\cdot\mathbf{BF_4}^{-}$. In addition, the value of the coupling constant of the C9−C10−C11 moiety of $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$ is similar to those of $\mathbf{3}^{+}\cdot\mathbf{ClO_4}^{-}$ [18] and $\mathbf{4}^{+}\cdot\mathbf{ClO_4}^{-}$,[18] suggesting the existence of the bond fixation of the seven-membered ring of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ and $\mathbf{16a}^{+}\cdot\mathbf{BF_4}^{-}$ due to the benzo and naphtho annulation. The benzo moiety of $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$ [$J_{7,8} = 8.0$ Hz, $J_{8,9} = 7.0$ Hz, $J_{9,10} = 8.0$ Hz] and the naphtho moiety of $\mathbf{16a}^{+}\cdot\mathbf{BF_4}^{-}$ [$J_{8,9} = 8.0$ Hz, $J_{9,10} = 6.5$ Hz, $J_{10,11} = 8.0$ Hz] show relatively smaller bond alternations as compared with those of $\mathbf{3}^{+}\cdot\mathbf{ClO_4}^{-}$ and $\mathbf{4}^{+}\cdot\mathbf{ClO_4}^{-}$, respectively. In contrast, the benzo moiety of $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$ [$J_{5,6} = 8.5$ Hz, $J_{6,7} = 7.0$ Hz, $J_{7,8} = 8.5$ Hz] shows a larger bond alternation as compared with those of $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$ and $\mathbf{16a}^{+}\cdot\mathbf{BF_4}^{-}$ and the coupling constants are similar to those of $\mathbf{3}^{+}\cdot\mathbf{ClO_4}^{-}$.

Single crystals of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ were obtained by recrystallization from CH_3CN/AcOEt. Thus, X-ray crystal analyses of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ were performed, and the ORTEP drawings are shown in Figure 5.[23] The counteranion (BF_4^-) in $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ is omitted for clarity. The planes of the phenyl groups in $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ are twisted at 77.8° and 85.9° against the plane of the pyrrole ring, respectively. Although the π-system of $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$ has a nearly planar structure, the π-system of $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$ shows large deformation from planarity like a helicene because of the steric repulsion between the C13H and C17═O2 double bonds. In both cations of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$, the bond length of N1−C1 is shorter than that of N1−C4, suggesting that the former bond has a larger bond order. In cation $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$, the bond lengths of C4−C5 and C8−C9 are much shorter than those of C5−C6, C7−C8, and C3−C9. Similarly, in cation $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$, the bond lengths of C4−C5 and C6−C7 are much shorter than those of C5−C6, C7−C8, and C3−C9. Furthermore, in both cations of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$, the bond lengths of C10−C11 and C12−C13 are shorter than that of C11−C12. These facts suggest the existence of bond alternation, as shown in the canonical structure of $\mathbf{12a,b}^{+}$−**B** (Figure 6). In addition, the differences in bond lengths of C10−C11−C12 in $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ are relatively smaller as compared with those in the seven-membered ring, suggesting the existence of a small contribution of the canonical structures of $\mathbf{12a,b}^{+}$−**C**. Furthermore, the differences in bond lengths of C10−C11−C12 in cation $\mathbf{12a}^{+}\cdot\mathbf{BF_4}^{-}$ are smaller as compared with those in $\mathbf{12b}^{+}\cdot\mathbf{BF_4}^{-}$. Thus, a contribution of the canonical structure of $\mathbf{12a}^{+}$−**C** would be larger than that of $\mathbf{12b}^{+}$−**C**. The features agree with the structures of $\mathbf{12a,b}^{+}\cdot\mathbf{BF_4}^{-}$ on the basis of inspection of the ^{1}H NMR.

The affinity of the carbocation toward hydroxide ions expressed by the pK_{R+} value is the most common criterion of carbocation stability.[24] The pK_{R+} values of cations $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ as well as that of naphtho[*b*]tropylium ion $\mathbf{4}^{+}$ were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH_3CN and are summarized in Table 1, along with those of the reference compounds $\mathbf{1}^{+}$,[7] $\mathbf{3}^{+}$,[10] and $\mathbf{5a}^{+}$.[12] Because a sharp titration curve for the neutralization of cation $\mathbf{12b}^{+}$ was not obtained, the pK_{R+} value was estimated to be ca. 0.5. In addition, the reaction of cation $\mathbf{4}^{+}$ with hydroxide in all-buffer solutions proceeded completely and the peak of cation $\mathbf{4}^{+}$ was not observed in all-buffer solutions; thus, the pK_{R+} value

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[23] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[24] Freedman, H. H. In *Carbonium Ions*; Olah, G. A., Schleyer, P., Eds.; Wiley-Insterscience: New York, 1973.

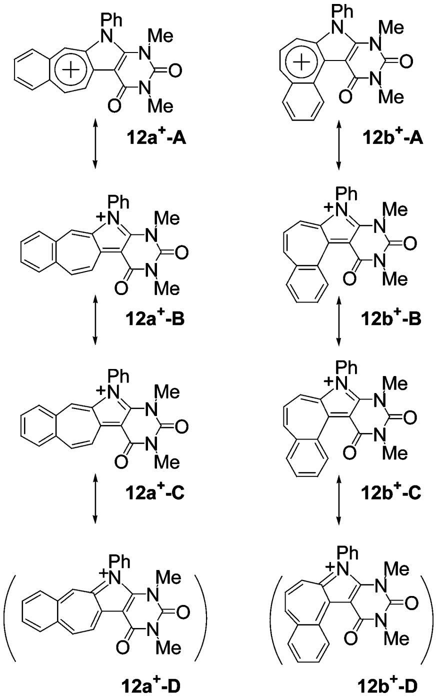

FIGURE 6. Resonance contributions for tropylium ions **12a**$^+$ and **12b**$^+$.

of cation **4**$^+$ was estimated to be <0. The pK_{R+} values are smaller, in the order **5a**$^+$ ($pK_{R+} = 10.9$) > **12a**$^+$ ($pK_{R+} = 9.0$) > **16a**$^+$ ($pK_{R+} = 6.3$), suggesting that the perturbation derived from the naphtho annulation is larger as compared with that from the benzo annulation. The feature is similar to those of cations **1**$^+$−**4**$^+$, and thus, cation **4**$^+$ would have a very small pK_{R+} value. In contrast, the pK_{R+} value of cation **12b**$^+$ (pK_{R+} = ca. 0.5) is much smaller.

The reduction potentials of cations **12a,b**$^+$ and **16a**$^+$ as well as those of cations **3**$^+$ and **4**$^+$ were determined by cyclic voltammentry (CV) in CH_3CN. The reduction waves were irreversible under the conditions of the CV measurements, and thus, the peak potentials are summarized in Table 1, together with those of the reference compounds **1**$^+$ [7] and **5a**$^+$.[12] The irreversible nature of **12a,b**$^+$ and **16a**$^+$ as well as that of cations **3**$^+$ and **4**$^+$ is probably due to the formation of a radical species and its dimerization, which is reported to be a typical property of uracil-annulated heteroazulenylium ions such as **5a**−**c**$^+$.[12−14] The $E1_{red}$ values are less negative in the order **5a**$^+$ > **12a**$^+$ > **12b**$^+$ > **16a**$^+$. Similarly, the $E1_{red}$ values are less negative in the order **1**$^+$ > **3**$^+$ > **4**$^+$, supporting that the perturbation derived from the naphtho annulation is larger as compared with that from the benzo annulation.

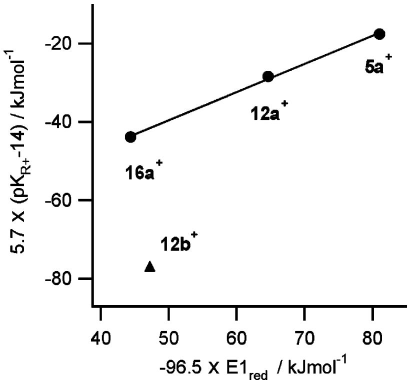

FIGURE 7. Plot of pK_{R+} values against $E1_{red}$ of **5a**$^+$**·BF**$_4^-$, **12a,b**$^+$**·BF**$_4^-$, and **16a**$^+$**·BF**$_4^-$.

The pK_{R+} values of cations **5a**$^+$, **12a,b**$^+$, and **16a**$^+$ are plotted against the $E1_{red}$ values of these cations (Figure 7). The units of $E1_{red}$ and pK_{R+} values were converted to kJ/mol [$-96.5 \times E1_{red}$/V and $5.7 \times (pK_{R+} - 14)$].[12,25,26] A good linear correlation line for **5a**$^+$, **12a**$^+$, and **16a**$^+$ was obtained, and the slope and *y*-intercept of this regression line were 0.72 and −75.439, respectively (correlation coefficient = 0.999). We have previously reported a similar correlation line obtained for cations **5a**−**d**$^+$, and the slope and *y*-intercept were obtained as 1.09 and −106.89, respectively;[12] thus, the slope of the regression line of cations **5a**$^+$, **12a**$^+$, and **16a**$^+$ is smaller than that of cations **5a**−**d**$^+$. Furthermore, the value is smaller than 1.0, suggesting that the more stable cation gives a less stable radical in a single-electron reduction of **5a**$^+$, **12a**$^+$, and **16a**$^+$.[25,26] The plot of **12b**$^+$ is placed at a far position from the regression line because of its very small pK_{R+} value, suggesting that the relation between $E1_{red}$ and pK_{R+} values is different from that of cations **5a**$^+$, **12a**$^+$, and **16a**$^+$. The feature would be attributable to the deformation of **12b**$^+$ from planarity arising from the steric repulsion: because the steric repulsion is reduced by the incorporation of OH^-, equilibrium between cation **12b**$^+$ and the corresponding alcohol would favor the alcohol. Thus, the pK_{R+} value of **12b**$^+$ would become smaller as compared with that expected for $E1_{red}$. This feature may also be ascribed to the instability of the corresponding alcohol under the conditions of the pK_{R+} measurement. Immediate (5 s) acidification of an alkaline solution (ca. pH 14) of **12b**$^+$ with TFA regenerated the absorption maxima of the cations in the visible regions in 91% yield.

Reactivitiy. To clarify the reactivity, the reactions of **12a,b**$^+$**·BF**$_4^-$ with some nucleophiles, $NaBH_4$ and diethylamine, were investigated. Although the reduction of **5a**−**d**$^+$**·BF**$_4^-$ with $NaBH_4$ proceeded at C5, C7, and C9 to give mixtures of three regioisomers,[12−14] the reduction of **12a**$^+$**·BF**$_4^-$ occurred at C11 to give a single product **19** in moderate yield (Scheme 3). Compound **19** was oxidized by DDQ to regenerate **12a**$^+$**·BF**$_4^-$ in good yield. On the other hand, a reaction of **12b**$^+$**·BF**$_4^-$ with $NaBH_4$ was carried out in an NMR tube to give a mixture of C9 adduct **20** and C11 adduct **21** in a ratio of 2:3. The formation of **19**−**21** would be ascribed to the stability of the closed pyrrolopyrimidine and benzene rings. The formation of the C11 adduct which predominates over the C9 adduct is similar to the reaction of **5a**$^+$**·BF**$_4^-$ with $NaBH_4$, in which the ratio of the C9 adduct was larger than those of the C5 and C7 adducts. In addition, compound **19** was used for the reduction of ethyl benzoylformate **24**; however, the reduction did not proceed and starting compounds **19** and **24** were recovered quantitatively. The low reactivity of **19** would be attributable to the lower stability of the corresponding cation **12a**$^+$**·BF**$_4^-$, and thus, benzo and naphtho annulations were not effective for the reducing ability.[27] Furthermore, reactions of **12a,b**$^+$**·BF**$_4^-$ with diethylamine in NMR tubes were carried out. The diethylamine addition of **12a**$^+$**·BF**$_4^-$ occurred at C11 to afford **22**, similar to

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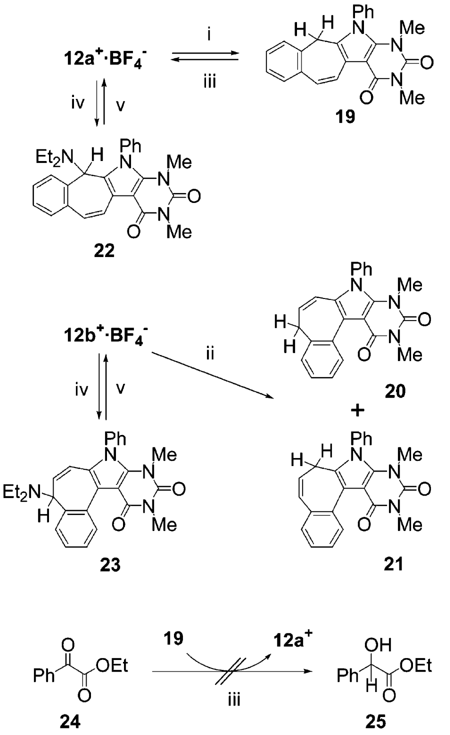
[25] Naya, S.; Nitta, M. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2427.

[26] Naya, S.; Sakakibara, T.; Nitta, M. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1032.

[27] Naya, S.; Nishimura, J.; Nitta, M. *J. Org. Chem.*, in press.

SCHEME 3[a]

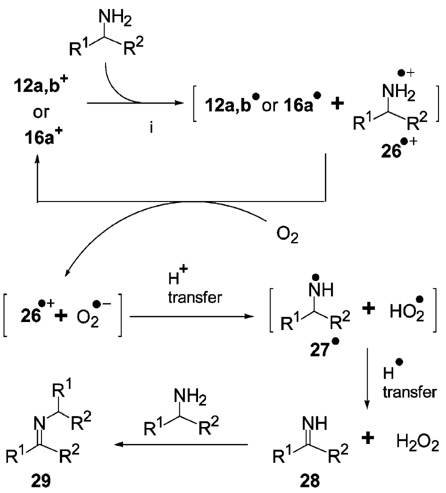


[a] Reagents and conditions: (i) NaBH$_4$, CH$_3$CN, room temperature, 2 h; (ii) NaBH$_4$, CD$_3$CN, room temperature, 2 h; (iii) (a) DDQ, CH$_2$Cl$_2$, room temperature, 2 h; (b) 42% aqueous HBF$_4$, Ac$_2$O, 0 °C, 1 h; (iv) diethylamine, CD$_3$CN, room temperature, 30 s; (v) 42% aqueous HBF$_4$, Ac$_2$O, 0 °C, 1 h; (vi) Mg(ClO$_4$)$_2$, CHCl$_3$, CH$_3$CN, 60 °C, 4 days.

the reaction with NaBH$_4$. In contrast, the reaction of **12b^{+}·BF$_4^{-}$** with diethylamine proceeded at only C9 to give **23** as a single product. The reaction of **5a^{+}·BF$_4^{-}$** with diethylamine proceeded at only C7,[16] and thus, the reactivity of **12b^{+}·BF$_4^{-}$** would be similar to that of **5a^{+}·BF$_4^{-}$**. Compounds **22** and **23** are stable in CD$_3$CN for a few days in the presence of diethylamine in the dark; however, they decompose during concentration in vacuo. Satisfactory ^{1}H and ^{13}C NMR were obtained for **22** and **23**; however, HRMS of **22** and **23** gave only the (M−NEt$_2$)$^+$ peaks instead of the M$^+$ peak. Upon treatment with 42% aqueous HBF$_4$ in Ac$_2$O, compounds **22** and **23** regenerated **12a,b^{+}·BF$_4^{-}$** in good yields, respectively.

Autorecycling Oxidation of Amines. We have previously reported that compounds **5a−d^{+}·BF$_4^{-}$** undergo autorecycling oxidation toward some alcohols and amines under photoirradiation.[12−15] In this context, we found that compounds **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$** have oxidizing ability toward benzylamine, 1-phenylethylamine, hexylamine, and cyclohexylamine to give the corresponding imines under aerobic and photoirradiation conditions. Imine R^{1}R^{2}C=NH was produced at first; however, it reacts with another amine to result in the formation of R^{1}R^{2}C=N−CHR^{1}R^2 (Scheme 4). Then, the reaction mixture was diluted with ether and filtered, and the filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound which is generated by hydrolysis of imine. The results are summarized in Table 2. Direct irradiation of the amines in the absence of **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$** (named "blank") gives the corresponding carbonyl compounds in low to modest yields upon similar treatments. Thus, the yields are calculated by subtraction of the blank yield from the yield of the carbonyl compound in the presence of **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$**. The recycling numbers are more than one (Table 2), and thus, autorecycling oxidation clearly proceeds; however, cyclohexylamine was not oxidized effectively by **12a^{+}·BF$_4^{-}$** (Table 2, run 4). In the oxidation of 1-phenylethylamine, hexylamine, and cyclohexylamine, the yield of the imine became higher in the order **12a^{+}·BF$_4^{-}$** < **12b^{+}·BF$_4^{-}$** < **16a^{+}·BF$_4^{-}$**, and thus, cation **16a^{+}·BF$_4^{-}$** would be more effective for the oxidation of amines.

SCHEME 4[a]



[a] Reagents and conditions: (i) $h\nu$, aerobic, CH$_3$CN, room temperature, 1 h.

TABLE 2. Autorecycling Oxidation of Some Amines by 12a,b^{+}·BF$_4^{-}$ and 16a^{+}·BF$_4^{-}$ under Photoirradiation[a]

run	compd	amine	yield/μmol[b,c]	recycling no.[d]
1	**12a^{+}·BF$_4^{-}$**	PhCH$_2$NH$_2$	83.9	16.8
2	**12a^{+}·BF$_4^{-}$**	PhCH(Me)NH$_2$	50.0	10.0
3	**12a^{+}·BF$_4^{-}$**	hexylamine	17.9	3.6
4	**12a^{+}·BF$_4^{-}$**	cyclohexylamine	0.0	0
5	**12b^{+}·BF$_4^{-}$**	PhCH$_2$NH$_2$	108.4	21.7
6	**12b^{+}·BF$_4^{-}$**	PhCH(Me)NH$_2$	52.9	10.6
7	**12b^{+}·BF$_4^{-}$**	hexylamine	42.9	8.6
8	**12b^{+}·BF$_4^{-}$**	cyclohexylamine	18.0	3.6
9	**16a^{+}·BF$_4^{-}$**	PhCH$_2$NH$_2$	88.1	17.6
10	**16a^{+}·BF$_4^{-}$**	PhCH(Me)NH$_2$	67.3	13.5
11	**16a^{+}·BF$_4^{-}$**	hexylamine	79.5	15.9
12	**16a^{+}·BF$_4^{-}$**	cyclohexylamine	29.5	5.9

[a] A CH$_3$CN (16 mL) solution of compound **12a,b^{+}·BF$_4^{-}$** or **16a^{+}·BF$_4^{-}$** (5 μmol) and amines (2.5 mmol, 500 equiv) was irradiated by RPR-100 350 nm lamps under aerobic conditions for 16 h. [b] Isolated by converting to the corresponding 2,4-dinitrophenylhydrazone. [c] The yield is calculated by subtraction of the "blank" yield from the total yield. [d] Recycling number of **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$**.

We propose that the present autorecycling oxidation proceeds via electron transfer from an amine to the excited compounds **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$**, as shown in Scheme 4.[15,28] The electron transfer from an amine to the excited state of **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$** would occur to produce radicals **12a,b$^{\bullet}$** and **16a$^{\bullet}$** and a cation radical **26$^{\bullet+}$**. On the other hand, there is also a possibility that the homolysis of the amine adducts, generated by the reaction of **12a,b^{+}·BF$_4^{-}$** and **16a^{+}·BF$_4^{-}$** with amines, by photoirradiation would afford radicals **12a,b$^{\bullet}$** and **16a$^{\bullet}$** directly. An electron transfer from radical species **12a,b$^{\bullet}$** and **16a$^{\bullet}$** to molecular oxygen may give the superoxide anion radical and **12a,b^{+}** and **16a^{+}** because tropyl radical

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(28) Naya, S.; Iida, Y.; Nitta, M. *Tetrahedron* **2004**, *60*, 459.

derivatives are known to be oxidized readily by molecular oxygen.[29] Then, a proton transfer from cation radical $\mathbf{26}^{\bullet+}$ to the superoxide anion radical may occur, followed by formation of the products **28** and H_2O_2. Compound **28** reacts with excess amine to give imine **29**.

Summary

A convenient preparation of novel areno-annulated 1,3-dimethyl-10-phenylcyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4-(1,3*H*)-dionylium ions $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ and $\mathbf{16a^{+}\cdot BF_4^{-}}$ was accomplished by three-step reactions starting from benzo[*b*]tropone **7** and naphtho[2,3-*d*]tropone **13** with 6-anilino-1,3-dimethyluracil **8**. Structural characteristics of $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ were clarified on inspection of the UV−vis and NMR spectral data as well as by X-ray crystal analyses. The stability of cations $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ is expressed by the pK_{R+} values which were determined spectrophotometrically as the values of ca. 0.5−9.0. In addition, the pK_{R+} value of naphtho[*b*]tropylium ion $\mathbf{4}^{+}$ was clarified to be much lower, at <0. The electrochemical reduction of $\mathbf{12a,b}^{+}$ and $\mathbf{16a}^{+}$ as well as that of benzotropylium ion $\mathbf{3}^{+}$ and cation $\mathbf{4}^{+}$ exhibited a reduction potential at −0.09 to −0.67 (V vs Ag/AgNO$_3$) upon cyclic voltammetry (CV). The reactivity of $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ with some nucleophiles, hydride and diethylamine, was clarified. Although the reactions of $\mathbf{12a^{+}\cdot BF_4^{-}}$ afforded C11 adduct **19** as a single product, the addition reactions of $\mathbf{12b^{+}\cdot BF_4^{-}}$ proceeded at both C9 and C11. The attempted reduction of methyl benzoylformate using **21** was carried out unsuccessfully. The photoinduced oxidation reaction of $\mathbf{12a,b^{+}\cdot BF_4^{-}}$ and $\mathbf{16a^{+}\cdot BF_4^{-}}$ toward some amines under aerobic conditions was carried out to give the corresponding imines with the recycling numbers of 3.6−21.7.

Experimental Section

Reaction of $\mathbf{3^{+}\cdot ClO_4^{-}}$ with 8. To a stirred solution of $\mathbf{3^{+}\cdot ClO_4^{-}}$ (482 mg, 2 mmol) and **8** (462 mg, 2 mmol) in CH_3CN (20 mL) at −40 °C was added NaH (80 mg, 2 mmol), and the mixture was stirred at −40 °C for 20 h. To the mixture was added saturated aqueous NaCl, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give a mixture of **9a** and **9b** (609 mg, 82%) in a ratio of 1:5.

Synthesis of 11b. A mixture of benzo[*b*]tropone **7** (46.8 mg, 0.3 mmol) and $CeCl_3\cdot 7H_2O$ (145.3 mg, 0.39 mmol) in the presence of molecular sieves (0.4 nm, 30 mg) in EtOH (14 mL) was stirred at room temperature for 5 min. To the solution was added $NaBH_4$ (24.9 mg, 0.66 mmol), and the mixture was heated under reflux for 4 h. To the resulting mixture was added saturated aqueous NaCl, and the mixture was extracted with PhH. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **11b** (52.6 mg, 94%).

Reaction of 8 with 11b. To a mixture of **8** (62.2 mg, 0.27 mmol) and **11b** (52.6 mg, 0.28 mmol) in the presence of molecular sieves (0.4 nm, 30 mg) in CH_3CN (9 mL) was added *p*-TsOH·2H$_2$O (5.4 mg, 0.028 mmol), and the mixture was stirred at room temperature for 6 h. To the mixture was added saturated aqueous NaCl, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give a mixture of **9a** and **9b** (98.6 mg, 99%, **9a**/ **9b** = 1:5).

Synthesis of $\mathbf{12a^{+}\cdot BF_4^{-}}$ and $\mathbf{12b^{+}\cdot BF_4^{-}}$. To a stirred solution of a mixture of **9a** and **9b** (600 mg, 1.62 mmol) in $CHCl_3$ (40 mL) was added DDQ (735 mg, 3.24 mmol), and the mixture was heated under reflux for 16 h. After evaporation of the solvent, the residue was dissolved in a mixture of Ac_2O (25 mL) and 42% aqueous HBF_4 (5 mL) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (150 mL), and the precipitates were collected by filtration and washed with Et_2O to give a mixture of $\mathbf{12a^{+}\cdot BF_4^{-}}$ and $\mathbf{12b^{+}\cdot BF_4^{-}}$. The mixture of $\mathbf{12a^{+}\cdot BF_4^{-}}$ and $\mathbf{12b^{+}\cdot BF_4^{-}}$ was recrystallized from CH_3CN/AcOEt to give crystals of $\mathbf{12b^{+}\cdot BF_4^{-}}$ (59 mg, 8%) and filtrate containing $\mathbf{12a^{+}\cdot BF_4^{-}}$. The filtrate was concentrated in vacuo and recrystallized from CH_3CN/Et_2O to give crystals of $\mathbf{12a^{+}\cdot BF_4^{-}}$ (220 mg, 30%).

Synthesis of 14. A mixture of naphtho[2,3-*d*]tropone **13** (137 mg, 0.67 mmol) and $CeCl_3\cdot 7H_2O$ (322 mg, 0.86 mmol) in the presence of molecular sieves (0.4 nm, 60 mg) in EtOH (35 mL) was stirred at room temperature for 5 min. To the solution was added $NaBH_4$ (55.3 mg, 1.46 mmol), and the mixture was heated under reflux for 5 h. To the resulted mixture was added saturated aqueous NaCl, and the mixture was extracted with PhH. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **14** (149 mg, 95%).

Synthesis of $\mathbf{4^{+}\cdot ClO_4^{-}}$. A mixture of Ac_2O (1 mL) and 60% aqueous $HClO_4$ (180 mg) was cooled to 0 °C. To the solution was added slowly a solution of **14** (39.8 mg, 0.167 mmol) in Et_2O (3 mL), and the mixture was stirred for 20 min. The generated precipitates were collected by filtration under an N_2 atmosphere to give $\mathbf{4^{+}\cdot ClO_4^{-}}$ (31.1 mg, 64%).

Reaction of 8 with 14. To a mixture of **8** (23.1 mg, 0.1 mmol) and **14** (23.6 mg, 0.1 mmol) in the presence of molecular sieves (0.4 nm, 10 mg) in CH_3CN (5 mL) was added *p*-TsOH·2H$_2$O (1.9 mg, 0.01 mmol), and the mixture was stirred at room temperature for 3 h. To the mixture was added saturated aqueous NaCl, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give a mixture of **15a** and **15b** (48.5 mg, 99%, **15a**/**15b** = 1:7).

Synthesis of $\mathbf{16a^{+}\cdot BF_4^{-}}$. To a stirred solution of a mixture of **15a** and **15b** (48.5 mg, 0.1 mmol) in $CHCl_3$ (4 mL) was added DDQ (45.4 mg, 0.2 mmol), and the mixture was heated under reflux for 16 h. After evaporation of the solvent, the residue was dissolved in a mixture of Ac_2O (25 mL) and 42% aqueous HBF_4 (5 mL) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (150 mL), and the precipitates were collected by filtration and washed with Et_2O to give $\mathbf{16a^{+}\cdot BF_4^{-}}$ (9.8 mg, 19%).

^{1}H NMR Monitoring of the Thermal Rearrangement of 15b. A solution of compound **15b** (4.2 mg, 0.01 mmol) in acid-free CD_3CN (0.5 mL) in the absence and presence of $CHCl_3$ (0.05 mL) was heated at 60 °C in an NMR tube. After 6 h, the NMR measurement was carried out to exhibit the formation of **8**, **15a**, and **15b** in a ratio of 0.03:1.40:1.00.

Modified Procedure for Synthesis of $\mathbf{16a^{+}\cdot BF_4^{-}}$. A solution of a mixture of **15a** and **15b** (100 mg, 0.238 mmol) in $CHCl_3$ (10 mL) containing HCl, which is generated by decomposition of $CHCl_3$, was heated under reflux for 6 h. To the resulted solution was added DDQ (108 mg, 0.476 mmol), and the mixture was heated under reflux for 16 h. After evaporation of the solvent, the residue was dissolved in a mixture of Ac_2O (25 mL) and 42% aqueous HBF_4 (5 mL) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (150 mL), and the precipitates were collected by filtration and washed with Et_2O to give $\mathbf{16a^{+}\cdot BF_4^{-}}$ (30.4 mg, 25%).

Determination of pK_{R+} Values of $\mathbf{12a,b}^{+}$, $\mathbf{16a}^{+}$, and $\mathbf{4}^{+}$. 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), $Na_2B_4O_7$ (0.025 M) and HCl (0.1 M) (for pH 8.2−9.0), and $Na_2B_4O_7$ (0.025 M) and NaOH (0.1 M) (for pH 9.2−10.8) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 6 mg of compounds $\mathbf{12a,b^{+}\cdot BF_4^{-}}$, $\mathbf{16a^{+}\cdot BF_4^{-}}$, and $\mathbf{4^{+}\cdot ClO_4^{-}}$ in CH_3CN (20 mL), were diluted to 10 mL with the buffer

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[29] (a) Jacobi, D.; Abraham, W.; Pischel, U.; Grubert, L.; Schnabel, W. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1241. (b) Jacobi, D.; Abraham, W.; Pischel, U.; Grubert, L.; Stösser, R.; Schnabel, W. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1695.

solution (8 mL) and CH_3CN (1 mL). The UV−vis spectrum was recorded for each cation, **12a,b$^+$·BF$_4^-$**, **16a$^+$·BF$_4^-$**, and **4$^+$·ClO$_4^-$**, in 20 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 wavelength (457 nm for **12a$^+$·BF$_4^-$**; 491 nm for **12b$^+$·BF$_4^-$**; 467 nm for **16a$^+$·BF$_4^-$**; and 599 nm for **4$^+$·ClO$_4^-$**) of each cation, **12a,b$^+$·BF$_4^-$**, **16a$^+$·BF$_4^-$**, and **4$^+$·ClO$_4^-$**, was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

Cyclic Voltammetry of Cations 3$^+$, 4$^+$, 12a,b$^+$, and 16a$^+$. A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference Ag/$AgNO_3$ electrode. Nitrogen was bubbled through a CH_3CN solution (4 mL) of each cation, **3$^+$·ClO$_4^-$**, **4$^+$·ClO$_4^-$**, **12a,b$^+$·BF$_4^-$**, and **16a$^+$·BF$_4^-$** (0.5 mmol dm^{-3}), and Bu_4NClO_4 (0.1 mmol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1}. Immediately after the measurements, ferrocene (0.1 mmol) ($E_{1/2} = +0.083$) was added as the internal standard, and the observed peak potential was corrected with reference to this standard. The cations **3$^+$·ClO$_4^-$**, **4$^+$·ClO$_4^-$**, **16a,b$^+$·BF$_4^-$**, and **20a$^+$·BF$_4^-$** exhibited reduction waves, and they are summarized in Table 1.

Reaction of 12a$^+$·BF$_4^-$ with NaBH$_4$. A solution of **12a$^+$·BF$_4^-$** (220 mg, 0.48 mmol) and $NaBH_4$ (54.4 mg, 1.44 mmol) in CH_3CN (20 mL) was stirred at room temperature for 2 h. To the mixture was added saturated aqueous NH_4Cl solution, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **19** (114 mg, 64%).

Oxidation of 19. To a stirred solution of **19** (36.9 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) was added DDQ (34.1 mg, 0.15 mmol), and the mixture was stirred at room temperature for 2 h. After evaporation of CH_2Cl_2, the residue was dissolved in a mixture of Ac_2O (5 mL) and 42% aqueous HBF_4 (1 mL) at 0 °C, and the mixture was stirred for another 1 h. To the mixture was added Et_2O (30 mL), and the precipitate was collected by filtration to give **12a$^+$·BF$_4^-$** (40.4 mg, 89%).

Reduction of 12b$^+$·BF$_4^-$ with NaBH$_4$ in CD$_3$CN. A solution of **12b$^+$·BF$_4^-$** (4.55 mg, 0.01 mmol) and $NaBH_4$ (1.13 mg, 0.03 mmol) in CD_3OD (0.5 mL) in an NMR tube was shaken at room temperature for 2 h, and the ^1H NMR spectrum of the solution of a mixture of **20** and **21** (**20**/**21** = 2:3) was recorded using Me_4Si as the internal standard.

Attempted Reduction of Ethyl Benzoylformate 24 Using 19. To a solution of **19** (36.9 mg, 0.1 mmol) and $Mg(ClO_4)_2$ (22 mg, 0.1 mmol) in $CHCl_3$ (10 mL) and CH_3CN (5 mL) was added **24** (17.8 mg, 0.1 mmol), and the mixture was heated at 60 °C for 4 days. The resulting mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated in vacuo to give the starting materials **19** (36.9 mg, 100%) and **24** (17.8 mg, 100%).

Reaction of 12a,b$^+$·BF$_4^-$ with Diethylamine in CD$_3$CN. To each solution of **12a,b$^+$·BF$_4^-$** (0.01 mmol) in CD_3CN (0.5 mL) in NMR tubes was added diethylamine (7.3 mg, 0.1 mmol). The NMR measurements were carried out immediately (after ca. 30 s).

Reaction of 22 and 23 with HBF$_4$. To each solution of **22** and **23**, prepared by the reaction of **12a,b$^+$·BF$_4^-$** (22.75 mg, 0.05 mmol) with diethylamine (7.3 mg, 0.1 mmol) in CH_3CN (20 mL), was added a mixture of acetic anhydride (5 mL) and 42% aqueous HBF_4 (1 mL) at 0 °C, and the mixture was stirred for 1 h. To the mixture was added Et_2O (50 mL), and the precipitate was collected by filtration to give **12a,b$^+$·BF$_4^-$** (**12a$^+$·BF$_4^-$** 16.3 mg, 72%; **12b$^+$·BF$_4^-$** 15.9 mg, 70%).

General Procedure for Autorecycling Oxidation of Amines in the Presence of 12a,b$^+$·BF$_4^-$ and 16a$^+$·BF$_4^-$. A CH_3CN (16 mL) solution of compound **12a,b$^+$·BF$_4^-$** (2.28 mg, 5 μmol) or **16a$^+$·BF$_4^-$** (2.53 mg, 5 μmol) and amines (2.5 mmol, 500 equiv) in a Pyrex tube was irradiated by RPR-100 350 nm lamps under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo, diluted with Et_2O, and filtered. The ^1H NMR spectra of the filtrates revealed the formation of the corresponding imines. The filtrate was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compounds. The results are summarized in Table 2.

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Supporting Information Available: Physical, analytical, and spectroscopic data of **4$^+$·ClO$_4^-$**, **9a,b**, **12a,b$^+$·BF$_4^-$**, **14**, **15a,b**, **16a$^+$·BF$_4^-$**, and **19**−**23**. ^1H and ^{13}C NMR spectra of **4$^+$·ClO$_4^-$**, **9a,b**, **12a,b$^+$·BF$_4^-$**, **14**, **15a,b**, **16a$^+$·BF$_4^-$**, and **19**−**23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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