

# Novel Synthesis, Properties, and Oxidizing Ability of 11,13-Disubstituted 3,8-Methanocycloundeca[8,9-*b*]pyrimido[5,4-*d*]furan-12(11*H*),14(13*H*)-dionylium Tetrafluoroborates

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Synthesis of novel 4,9-methanoundecafulvene [5-(4,9-methanocycloundeca-2',4',6',8',10'-pentaenylidene)pyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione] derivatives **10a–c** was accomplished. Their structural characteristics were investigated on the basis of the <sup>1</sup>H and <sup>13</sup>C NMR and UV–vis spectra. Upon treatment with DDQ, **10a–c** underwent oxidative cyclization to give novel 11,13-disubstituted 3,8-methanocycloundeca[8,9-*b*]pyrimido[5,4-*d*]furan-12(11*H*),14(13*H*)-dionylium tetrafluoroborates **11a–c·BF<sub>4</sub><sup>–</sup>** in good yields. The spectroscopic properties of **11a–c·BF<sub>4</sub><sup>–</sup>** were studied, and the structural characterization of **11b·BF<sub>4</sub><sup>–</sup>** was performed by the X-ray crystal analysis. Cations **11a–c** were very stable, and their p*K<sub>R</sub>*<sup>+</sup> values were determined spectrophotometrically to be 8.3–8.9. The electrochemical reduction of **11a–c** exhibited low reduction potentials at –0.43 to –0.45 (V vs Ag/AgNO<sub>3</sub>) upon cyclic voltammetry (CV). In a search for reactivity, reactions of **11a·BF<sub>4</sub><sup>–</sup>** with some nucleophiles, hydride and diethylamine, were carried out to clarify that the methano-bridge controls the nucleophilic attacks to occur with endo-selectivity. The photoinduced oxidation reactions of **11a·BF<sub>4</sub><sup>–</sup>** toward some amines under aerobic conditions were carried out to give the corresponding carbonyl compounds in more than 100% yield.

## Introduction

Flavins are known to play an important role as cofactors in a wide variety of biological redox reactions.<sup>1</sup> The flavin-redox systems have been investigated extensively through synthetic model systems and theoretical calculations.<sup>2</sup> Among these, 5-deazaflavins<sup>3</sup> and 5-deaza-10-oxaflavins<sup>4</sup> (2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-diones) have been studied extensively in the hope of providing mechanistic insight into flavin-catalyzed reactions. On the basis of the above observations, we have previously studied convenient preparations of 6-substituted 9-methylcyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),-10(9*H*)-diones and 9-methylcyclohepta[*b*]pyrimido[5,4-

*d*]furan-8,10(9*H*)-dione, which are the structural isomers of 5-deazaflavin and 5-deaza-10-oxaflavin, respectively, and their ability in oxidizing some alcohols to the corresponding carbonyl compounds.<sup>5,6</sup> In this relation, we have recently reported the oxidative cyclization of novel heptafulvenes **1a–c** by using DDQ to afford cyclohepta[*b*]pyrimido[5,4-*d*]furan-8(7*H*),10(9*H*)-dionylium tetrafluoroborates **2a–c·BF<sub>4</sub><sup>–</sup>** (Figure 1).<sup>7</sup> Furthermore, alternative synthesis, properties, and reactivity of **2a·BF<sub>4</sub><sup>–</sup>**<sup>8</sup> and its sulfur and nitrogen analogues **3a–c·BF<sub>4</sub><sup>–</sup>**<sup>8–10</sup> as well as their novel photoinduced autorecycling oxidizing reactions toward some alcohols were investigated. Thus, structural modifications of the uracil-annulated heteroazulenes such as **2a·BF<sub>4</sub><sup>–</sup>** and **3a–c·BF<sub>4</sub><sup>–</sup>** are a very interesting project from the viewpoint of exploration of novel functions. Much of the motivation for studying the properties of organic molecules stems from manipulation of the primary chemical structure. Strategies for raising or lowering the HOMO and LUMO levels include conjugation length control, as well as the introduction of an electron-withdrawing or -donating group to the parent molecular skeleton. Based on this concept, we have now embarked on investigation of the synthesis of 11, 13-

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(1) Muller, F. In *Chemistry and Biochemistry of Flavoenzymes*; Muller, F., Ed.; CRC Press: Boca Raton, 1991; Vol. 1, p 1 and references therein.

(2) (a) Chiu, C. C.; Pan, K.; Jordan, F. *J. Am. Chem. Soc.* **1995**, *117*, 7027. (b) Kim, J.; Hoegy, S. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 100. (c) Murahashi, S.; Ono, S.; Imada, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 2366. (d) Bergstad, K.; Jonsson, S.; Bächvall, J. *J. Am. Chem. Soc.* **1999**, *121*, 10424. (e) Van Houten, K. A.; Kim, J.; Bogdan, M. A.; Ferri, D. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 5864. (f) Zheng, Y.; Ornstein, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 9402. (g) Breinlinger, E. C.; Keenan, C. J.; Rotello, V. M. *J. Am. Chem. Soc.* **1998**, *120*, 8606. (h) Hasford, J. J.; Rizzo, C. J. *J. Am. Chem. Soc.*, **1998**, *120*, 2251. (i) Antony, J.; Medvedev, D. M.; Stuchebrukhov, A. A. *J. Am. Chem. Soc.* **2000**, *122*, 1057.

(3) Yoneda, F.; Kokel, B. In *Chemistry and Biochemistry of Flavoenzymes*; Muller, F., Ed.; CRC Press: Boca Raton, 1991; Vol. 1, p 121 and references therein.

(4) Yoneda, F.; Hirayama, R.; Yamashita, M. *Chem. Lett.* **1980**, 1157.

(5) Nitta, M.; Tajima, Y. *Synthesis* **2000**, 651.

(6) Takayasu, T.; Mizuta, Y.; Nitta, M. *Heterocycles* **2001**, *54*, 601.

(7) Naya, S.; Nitta, M. *Tetrahedron* **2003**, *59*, 3709.

(8) Naya, S.; Miyama, H.; Yasu, K.; Takayasu, T.; Nitta, M. *Tetrahedron* **2003**, *59*, 1811.

(9) Naya, S.; Miyama, H.; Yasu, K.; Takayasu, T.; Nitta, M. *Tetrahedron* **2003**, *59*, 4929.

(10) Naya, S.; Nitta, M. *Tetrahedron* **2003**, *59*, 7291.

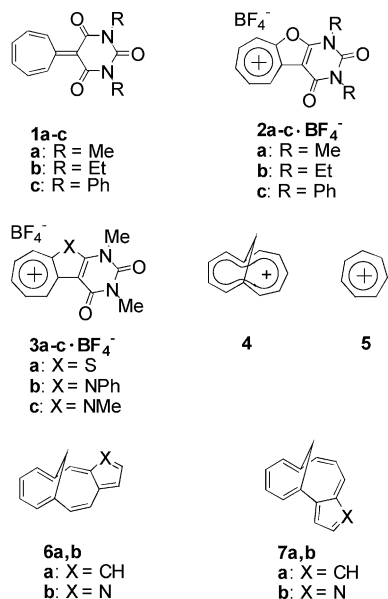


FIGURE 1.

disubstituted 3,8-methanocycloundeca[8,9-*b*]pyrimido[5,4-*d*]furan-12(11*H*),14(13*H*)-dionylium tetrafluoroborates **11a-c**·BF<sub>4</sub><sup>-</sup> (Scheme 1) for the first time, which are vinylogous compounds of **2a-c**, to involve 1,6-methano[11]annulenyl cation **4** instead of tropylium ion **5**. The 1,6-methano[11]annulenyl cation **4**, which is an aromatic 10π-electron analogue of the tropylium ion **5**, has high thermodynamic stability ( $pK_{R^+} = 6.2$ )<sup>11</sup> as compared with tropylium ion **5** ( $pK_{R^+} = 3.9$ ).<sup>12</sup> Thus, cations **11a-c**·BF<sub>4</sub><sup>-</sup> are expected to have extended π-conjugation and higher thermodynamic stability. As for methano-bridged aromatic compounds having 14π-electron (azulene and 1-heteraazulene vinylogues), Prinzbach et al.<sup>13</sup> and our research group<sup>14</sup> have reported on a series of 5,10-methanocyclopentacycloundecene ring system **6a** and 4,9-methanocyclopentacycloundecene ring system **7a** as vinylogous compounds of azulene, respectively. We have also reported the synthesis and spectroscopic properties of 6,11- and 4,9-methanocycloundeca[*b*]pyrrole ring systems **6b** and **7b** as 1-azaazulene vinylogues.<sup>15</sup> Regarding these compounds, the chemical shifts of the methano-bridge protons and carbon can conveniently evaluate their aromaticity.<sup>16,17</sup> In addition, since the methano-bridge can become a planar-chiral source, the synthesis and resolution of chiral methano-bridge compounds have

(11) (a) Grimme, W.; Hoffmann, H.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 354. (b) Vogel, E.; Feldmann, R.; Düwel, H. *Tetrahedron Lett.* **1970**, *1*, 1941.

(12) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011 and references therein.

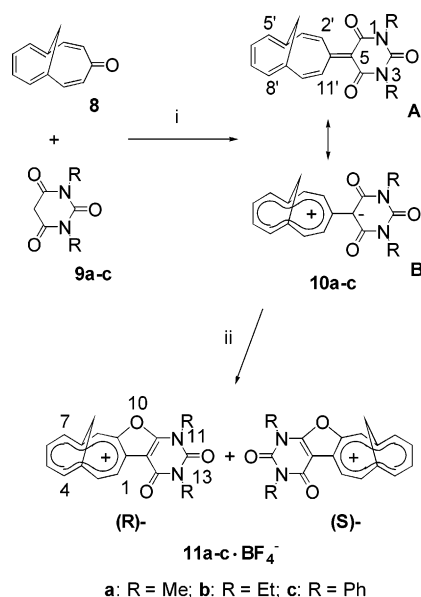
(13) (a) Prinzbach, H.; Knothe, L. *Pure Appl. Chem.* **1986**, *58*, 25. (b) Beck, A.; Hunkler, D.; Prinzbach, H. *Tetrahedron Lett.* **1984**, *25*, 1785.

(14) (a) Takayasu, T.; Nitta, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3255. (b) Nitta, M.; Akaogi, A.; Tomioka, H. *Heterocycles* **2003**, *60*, 365.

(15) Kanomata, N.; Kamae, K.; Iino, Y.; Nitta, M. *J. Org. Chem.* **1992**, *57*, 5313.

(16) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145. (b) Cremer, D.; Dick, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 865 and references therein.

(17) (a) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, *8*, 3239. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216. (c) Scott, L. T.; Sumpster, C. A.; Oda, M.; Erden, I. *Tetrahedron Lett.* **1989**, *30*, 305.

SCHEME 1<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) Ac<sub>2</sub>O, 120 °C, 1.5 h; (ii) (a) DDQ, CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h, (b) 42% aq HBF<sub>4</sub>, Ac<sub>2</sub>O, 0 °C, 1 h.

appeared.<sup>18</sup> From this viewpoint, the preparation and resolution of chiral **11a-c**·BF<sub>4</sub><sup>-</sup> are also interesting in relation to their functions. Thus, we studied the two-step synthesis, properties, and oxidizing ability of novel 11,13-disubstituted 3,8-methanocycloundeca[8,9-*b*]pyrimido[5,4-*d*]furan-12(11*H*),14(13*H*)-dionylium tetrafluoroborates **11a-c**·BF<sub>4</sub><sup>-</sup>, which were characterized on the basis of the spectral data and  $pK_{R^+}$  as well as redox potentials. The detailed structural characterization of **11b** was also carried out by X-ray crystal analysis. The photoinduced autorecycling oxidation of alcohols and amines to give the corresponding carbonyl compounds is studied as well.

## Results and Discussion

**Synthesis.** The synthetic strategy of **11a-c** is, at first, to obtain 4,9-methanoundecafulvene [5-(4,9-methanocycloundeca-2',4',6',8',10'-pentaenylidene)pyrimidine-2(1*H*),4-(3*H*),6(5*H*)-trione] derivatives **10a-c** followed by oxidative cyclization.<sup>7</sup> Condensation reactions of 4,9-methano[11]annulenone **8**<sup>19</sup> with disubstituted barbituric acids **9a-c** in Ac<sub>2</sub>O under reflux afforded **10a-c** as orange or reddish needles in moderate to good yields (Scheme 1). Compounds **10a-c** have a C<sub>s</sub> symmetry, and thus, **10a-c** are apparently achiral compounds. Oxidation reactions of **10a-c** with DDQ in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and subsequent anion-exchange reaction by using 42% aq HBF<sub>4</sub> in Ac<sub>2</sub>O afforded possible racemic compounds, **11a-c**·BF<sub>4</sub><sup>-</sup> in good yields. The results are summarized in Table 1. Apparently, the oxidative cyclization at the C-2' position of **10a-c** gives (**R**)-**11a-c**·BF<sub>4</sub><sup>-</sup>, while the cyclization at the C-11' position affords

(18) (a) Chen, L.; Ding, K.; Tian, W. *Chem. Commun.* **2003**, 838. (b) Marshall, J. A.; Conrow, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 4274. (c) Marshall, J. A.; Conrow, R. E. *J. Am. Chem. Soc.* **1983**, *105*, 5679. (d) Meyer, A.; Schlögl, K.; Lerch, U.; Vogel, E. *Chem. Ber.* **1988**, *121*, 917. (e) Schlögl, K.; Widhalm, M. *Chem. Ber.* **1982**, *115*, 3042.

(19) Vogel, E. *23rd Int. Congr. Pure Appl. Chem.* **1971**, *1*, 275.

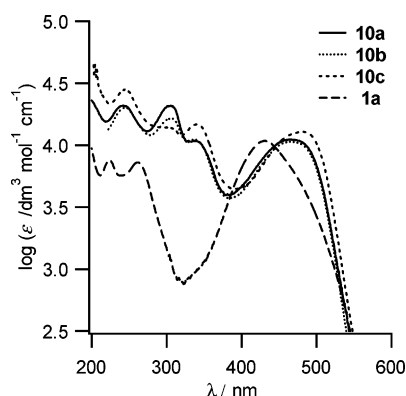


FIGURE 2. UV-vis spectra of **10a–c** and **1a** in  $\text{CH}_3\text{CN}$ .

TABLE 1. Results for the Preparation of **10a–c** and Cations **11a–c**· $\text{BF}_4^-$

run	compd	condensation		oxidative cyclization	
		product	yield (%)	product	yield (%)
1	<b>9a</b>	<b>10a</b>	81	<b>11a</b> · $\text{BF}_4^-$	100
2	<b>9b</b>	<b>10b</b>	53	<b>11b</b> · $\text{BF}_4^-$	100
3	<b>9c</b>	<b>10c</b>	66	<b>11c</b> · $\text{BF}_4^-$	95

TABLE 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectral Data and Redox Potentials of Methanoundecafulvenes **10a–c** and Reference Compounds **1a–c**

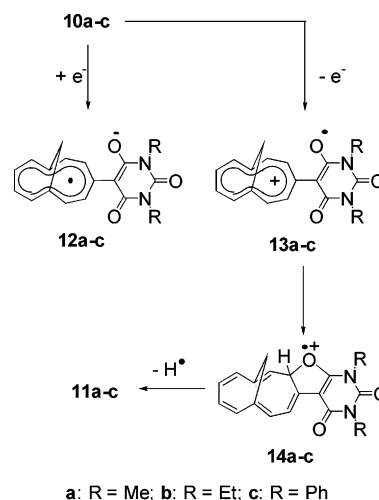
compd	NMR		redox potential <sup>a</sup>	
	$^1\text{H}/\delta$	$^{13}\text{C}/\delta^d$	$E_{1,\text{red}}$	$E_{1,\text{ox}}$
<b>10a</b>	7.12 <sup>b</sup>	110.5	−1.19	+0.78
<b>10b</b>	7.11 <sup>b</sup>	109.4	−1.14	+0.90
<b>10c</b>	7.30 <sup>b</sup>	108.0	−1.14	+0.84
<b>1a</b> <sup>e</sup>	9.20 <sup>c</sup>	102.7	−1.23	+1.07
<b>1b</b> <sup>e</sup>	9.14 <sup>c</sup>	103.1	−1.25	+1.07
<b>1c</b> <sup>e</sup>	9.38 <sup>c</sup>	101.9	−1.18	+1.10

<sup>a</sup> V vs  $\text{Ag}/\text{AgNO}_3$ ; cathodic peak potential. <sup>b</sup> H-2', 11'. <sup>c</sup> H-2', 7'. <sup>d</sup> C-5 of the barbitric acid moiety. <sup>e</sup> Reference 7.

(*S*)-**11a–c**· $\text{BF}_4^-$ . Thus, the oxidative cyclization results in the formation of racemic compounds (*R*),(*S*)-**11a–c**· $\text{BF}_4^-$ . Unfortunately, attempted optical resolution by means of recrystallization and conversion to diastereomers by adding chiral amine is unsuccessful at the present stage (vide infra). Thus, racemic compounds (*R*),(*S*)-**11a–c**· $\text{BF}_4^-$  are represented as **11a–c**· $\text{BF}_4^-$ . Compounds **10a–c** and **11a–c**· $\text{BF}_4^-$  were fully characterized on the basis of the  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, UV-vis, and mass spectral data, as well as elemental analyses.

**Properties.** The UV-vis spectra of **10a–c** in  $\text{CH}_3\text{CN}$  are shown in Figure 2, together with those of reference compounds **1a**.<sup>7</sup> The spectra of **10a–c** resemble each other, and the longest wavelength absorption maxima appear at 488 nm (**10a**), 488 nm (**10b**), and 493 nm (**10c**). These values are longer by ca. 50 nm than those of **1a**, suggesting the elongated  $\pi$ -conjugation of compounds **10a–c** as compared with those of **1a–c**.<sup>7</sup> In the  $^{13}\text{C}$  NMR spectra, signals of the carbon atom (C-5) of the barbitric acid moiety in **10a–c** appear at low field ( $\delta_{\text{C}}$  108.0–110.5), suggesting the low electron density as compared with those of **1a–c** ( $\delta_{\text{C}}$  101.7–103.1) (Table 2).<sup>7</sup> Thus, contribution of the zwitterionic canonical structure **B** of **10a–c** seems to be less important as compared with the canonical structure **A**; however, the 1,6-methano[11]-

SCHEME 2



annulenyl cation **4** ( $pK_{\text{R}^+}$ , 6.2)<sup>11</sup> is more stable than tropylium ion **7** ( $pK_{\text{R}^+}$ , 3.9).<sup>12</sup> This feature is similar to the cases of dicyano-substituted heptafulvene and 4,9-methanoundecafulvene; the C-12 carbon signal of 12,12-dicyano-4,9-methanoundecafulvene ( $\delta_{\text{C}}$  83.6)<sup>20</sup> is shifted to lower field as compared with the C-8 carbon signal of 8,8-dicyanoheptafulvene ( $\delta_{\text{C}}$  70.1).<sup>21</sup> Moreover, the proton signals of the H-2' and the H-11' of **10a–c** appearing at  $\delta$  7.11–7.30 are remarkably shifted to higher field as compared with those of **1a–c** ( $\delta$  9.14–9.38).<sup>7</sup> These features are ascribed to the bending structure of the 11-membered ring of compounds **10a–c**, which do not allow the H-2' and the H-11' to locate in the deshielding region of the carbonyl groups in the barbitric acid moiety. The redox property of **10a–c** was determined by cyclic voltammetry (CV) in acetonitrile. The oxidation and reduction waves of **10a–c** were irreversible under the conditions of CV measurements, and thus, the peak potentials are summarized in Table 2. The redox processes of **10a–c** are depicted in Scheme 2. At the first reduction potentials ( $E_{1,\text{red}}$ ) of **10a–c**, radical anions **12a–c** would be generated. On the other hand, radical cations **13a–c** seem to be generated at the first oxidation potentials ( $E_{1,\text{ox}}$ ). While the values ( $E_{1,\text{red}}$ ) of **10a–c** are more positive in the order **10a** < **10b** = **10c**, the values ( $E_{1,\text{ox}}$ ) of **10a–c** are more positive in the order **10a** > **10c** > **10b**. The first reduction potentials ( $E_{1,\text{red}}$ ) of **10a–c** are more positive than those of **1a–c**,<sup>7</sup> while the first oxidation potentials ( $E_{1,\text{ox}}$ ) of **10a–c** are more negative than those of **1a–c**.<sup>7</sup> These features suggest that compounds **10a–c** have the elongated  $\pi$ -conjugation as vinylogous compounds of **1a–c**. After the first cycle of CV measurements of **10a–c**, other reduction waves were recorded at −0.43, −0.39, and −0.46 V, respectively. These waves are suggested to be the reduction waves of **11a–c**, which are generated by oxidative cyclization reactions of **10a–c** under CV measurement. This feature is similar to the behavior of compounds **1a–c**.<sup>7</sup> Thus, DDQ-prompted oxidative cyclization of **10a–c** affording cations **11a–c** would proceed via a pathway similar to that of compounds **1a–c**. The

(20) Knothe, L.; Prinzbach, H. *Liebigs. Ann. Chem.* **1977**, 687.

(21) (a) Ikeda, Y.; Yin, B. Z.; Kato, N.; Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1996**, 69, 1319. (b) Ikeda, Y.; Yin, B. Z.; Kato, N.; Mori, A.; Takeshita, H.; *Chem. Lett.* **1992**, 1453. (c) Ikeda, Y.; Yin, B. Z.; Kato, N.; Mori, A.; Takeshita, H. *Heterocycles* **1993**, 36, 1725.

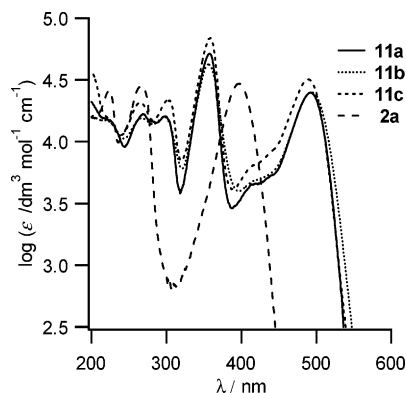


FIGURE 3. UV-vis spectra of **11a–c** and **2a** in  $\text{CH}_3\text{CN}$ .

radical cations **13a–c**, which are generated by one-electron oxidation of **10a–c**, undergo cyclization reaction to give intermediates **14a–c**, the hydrogen abstraction of which give cations **11a–c**. Subsequent anion exchange reaction with aq  $\text{HBF}_4$  solution results in the formation of cations **11a–c·BF<sub>4</sub><sup>-</sup>**.

In a similar fashion, cations **11a–c·BF<sub>4</sub><sup>-</sup>** were fully characterized on the basis of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, UV-vis, and mass spectral data, as well as elemental analyses. Mass spectra of these compounds exhibited the correct  $\text{M}^+ - \text{BF}_4^-$  ion peaks, which are indicative of the cationic structures of these compounds. The characteristic absorption bands for the counterion of  $\text{BF}_4^-$  were observed at  $1084\text{ cm}^{-1}$  in the IR spectra of these compounds, respectively. The UV-vis spectra of **11a–c·BF<sub>4</sub><sup>-</sup>** in  $\text{CH}_3\text{CN}$  are shown in Figure 3, together with those of **2a·BF<sub>4</sub><sup>-</sup>**. The spectra of **11a–c·BF<sub>4</sub><sup>-</sup>** resemble each other, and the longest wavelength absorption maxima show a red-shift by ca. 80 nm as compared with those of **2a·BF<sub>4</sub><sup>-</sup>**, suggesting the elongated  $\pi$ -conjugation of **11a–c·BF<sub>4</sub><sup>-</sup>**. The  $^1\text{H}$  NMR spectra of cations **11a–c·BF<sub>4</sub><sup>-</sup>** are noteworthy, since the chemical shifts of bridged-annulene systems are quite useful in determining such structural properties as diatropicity and bond alternation. Unambiguous proton assignment was made by analyzing  $^1\text{H}$  NMR, H–H COSY, and NOE spectra. Since a similar tendency is observed in a series of **11a–c·BF<sub>4</sub><sup>-</sup>**, the chemical shifts of the bridge protons and selected coupling constants of the peripheral protons of **11a·BF<sub>4</sub><sup>-</sup>** are shown in Figure 4 together with those of the reference compounds **10a**, **15**,<sup>22</sup> and **16**.<sup>15</sup> The large geminal coupling constant of the methylene protons ( $J_{\text{E,Z}} = 11.5\text{ Hz}$ ) supports the absence of a norcaradiene structure for **11a·BF<sub>4</sub><sup>-</sup>**. The bridge protons of **11a·BF<sub>4</sub><sup>-</sup>** appear at very high field ( $\delta -0.42$  and  $\delta -1.20$ ), and the peripheral protons appear in the aromatic region ( $\delta 8.39$ – $9.78$ ), suggesting a large diatropic ring current.<sup>23</sup> The differences in vicinal coupling constants in **11a·BF<sub>4</sub><sup>-</sup>** are smaller than those found in **10a** and **15**, suggesting that the bond alternation of **11a·BF<sub>4</sub><sup>-</sup>** is smaller than those of **10a** and **15**. While the vicinal coupling constants in **11a·BF<sub>4</sub><sup>-</sup>** and **16** are similar, the chemical shifts of the bridge protons of **11a·BF<sub>4</sub><sup>-</sup>** are even higher than those of **16**.

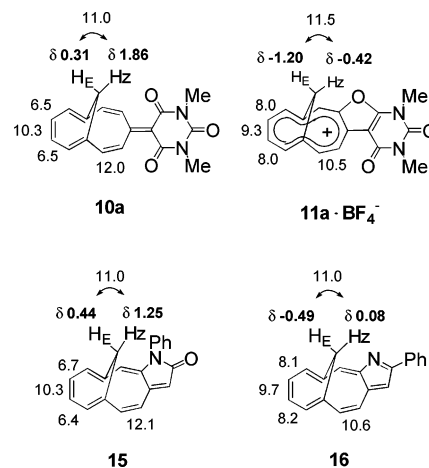


FIGURE 4. Chemical shifts and coupling constants of **10a**, **11a·BF<sub>4</sub><sup>-</sup>**, **15**, and **16**.

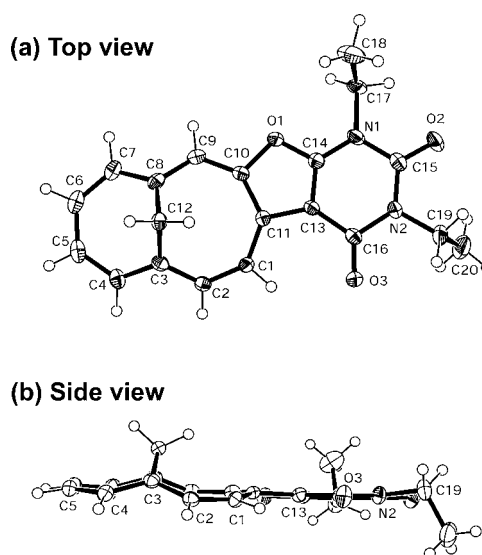


FIGURE 5. ORTEP drawing of **11b·BF<sub>4</sub><sup>-</sup>** with thermal ellipsoid plot (50% probability). Selected bond lengths (Å): O1–C10, 1.403(3); O1–C14, 1.332(3); C1–C2, 1.361(4); C1–C11, 1.421(3); C2–C3, 1.392(4); C3–C4, 1.402(4); C4–C5, 1.383(4); C5–C6, 1.409(4); C6–C7, 1.388(4); C7–C8, 1.386(4); C8–C9, 1.388(4); C9–C10, 1.364(4); C10–C11, 1.435(3); C11–C13, 1.417(4); C13–C14, 1.363(3); C14–N1, 1.322(3).

Destro and Simonetta have reported that 1,6-methano-[11]annulenylium ion **4** is described as a delocalized  $10\pi$ -electron system rather than a homotropylium ion.<sup>24</sup> A single crystal of **11b·BF<sub>4</sub><sup>-</sup>** was obtained by recrystallization from  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ , and thus, X-ray structure analysis was carried out and the ORTEP drawing of **11b·BF<sub>4</sub><sup>-</sup>** is shown in Figure 5. Although solvent molecules ( $\text{CH}_3\text{CN}$ ) exist in the single crystal, the solvent molecule and counteranion are omitted for clarity in the ORTEP drawing. The single crystal is a racemic mixture, and not conglomerate, and thus, optical resolution through recrystallization seems to be difficult (vide supra). The compound **11b·BF<sub>4</sub><sup>-</sup>** has a nearly planar structure, and selected bond lengths of **11b** obtained by X-ray analysis are also summarized in Figure 5. The bond lengths of C4–C5 and C6–C7 are shorter than those of C3–C4,

(22) Nitta, M.; Naya, S. *J. Chem. Res., Synop.* **1998**, 522–523; *J. Chem. Res., Miniprint* **1998**, 2363–2380.

(23) Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, 21, 113.

(24) Destro, R.; Simonetta, M. *Acta Crystallogr.* **1979**, B35, 1846.

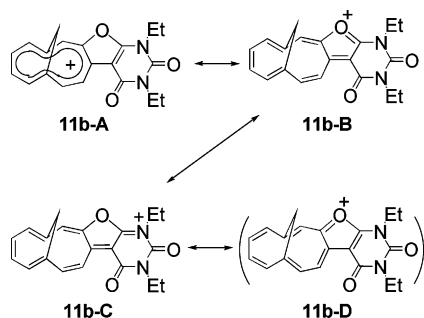


FIGURE 6.

TABLE 3.  $pK_{R+}$  Values and Reduction Potentials of Cations **11a–c**<sup>a</sup> and Reference Compounds **2a–c**, **4**, and **5**

compd	$pK_{R+}$	reduction potential <sup>b</sup>	
		$E1_{red}$	$E2_{red}$
<b>11a</b>	8.7	−0.43	
<b>11b</b>	8.3	−0.44	
<b>11c</b>	8.9	−0.45	−1.09
<b>2a</b> <sup>c</sup>	ca. 6.0	−0.58	
<b>2b</b> <sup>d</sup>		−0.61	
<b>2c</b> <sup>d</sup>		−0.58	
<b>4</b> <sup>e</sup>	6.2		
<b>5</b> <sup>f</sup>	3.9	−0.51	

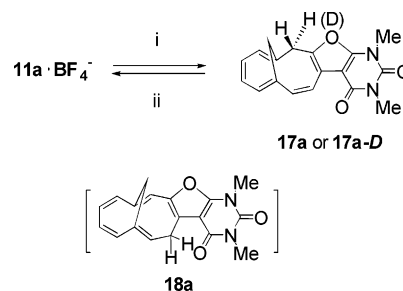
<sup>a</sup> Salts **11a–c**· $BF_4^-$  are used for the measurement. <sup>b</sup> V vs Ag/AgNO<sub>3</sub>; cathodic peak potential. <sup>c</sup> Reference 8. <sup>d</sup> Reference 7. <sup>e</sup> Reference 11. <sup>f</sup> Reference 12.

C5–C6, and C7–C8. This feature is similar to those of 1,6-methano[11]annulenyl cation **4**,<sup>24</sup> and the large transannular distance between C3 and C8 (**11b**: 2.32 Å; cf. 2.30 Å for **4**) also indicates that the homoconjugation is not important in this cation. The bond lengths of C1–C2 and C9–C10 are much shorter than those of C11–C1, C2–C3, and C8–C9, suggesting the canonical structures **11b–B** and **11b–C** are important for **11b** (Figure 6). In addition, since the bond length of O1–C14 is shorter than that of O1–C10, a contribution of **11b–D** seems to be less important. MO calculation of **11a** was carried out by the 6-31G\* basis set of the MP2 levels.<sup>25</sup> The bond length alternation obtained by MO calculation for **11a** is similar to that obtained by X-ray analysis for **11b**.

The affinity of the carbocation toward hydroxide ions expressed by the  $pK_{R+}$  value is the most common criterion of carbocation stability.<sup>26</sup> The  $pK_{R+}$  values of cations **11a–c** were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH<sub>3</sub>CN and are summarized in Table 3, along with those of reference compounds **2a**,<sup>8</sup> **4**,<sup>11</sup> **5**.<sup>12</sup> The  $pK_{R+}$  values of **11a–c** were

(25) Gaussian 98, revision A.11: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 2001.

(26) Freedman, H. H. *Carbonium Ions*; Olah, G. A., Schleyer, P., Eds.; Wiley-Interscience: New York, 1973.

SCHEME 3<sup>a</sup>

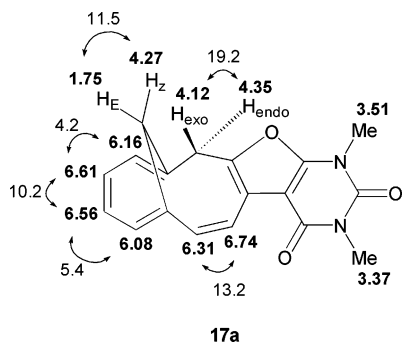
<sup>a</sup> Reagents and conditions: (i) NaBH<sub>4</sub>, CH<sub>3</sub>CN, rt, 1 h; (ii) (a) DDQ, CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h, (b) 42% aq HBF<sub>4</sub>, Ac<sub>2</sub>O, 0 °C, 1 h.

determined to be 8.3–8.9, which are much larger than those of **2a**, **4**, **5**. In addition, the  $pK_{R+}$  values are larger in the order **11b** < **11a** < **11c**. The  $pK_{R+}$  value difference between **11a** and **2a** is ca. 2.7 pH unit, which is similar to the difference between 1,6-methano[11]annulenyl cation **4** ( $pK_{R+}$  6.2)<sup>11</sup> and tropylium ion **5** ( $pK_{R+}$  3.9).<sup>12</sup>

The reduction potentials of **11a–c** were determined by cyclic voltammetry (CV) in CH<sub>3</sub>CN. The reduction waves of **11a–c** were irreversible under the conditions of the CV measurements; the peak potentials are summarized in Table 3, together with those of the reference compounds **2a–c**<sup>7</sup> and **5**.<sup>12</sup> The values ( $E1_{red}$ ) are more negative in the order **11a** > **11b** > **11c**. The  $E1_{red}$  of **11a–c** are more positive by 0.15, 0.17, and 0.13 V than those of **2a–c**, respectively. The irreversible nature is probably due to the formation of a radical species and its dimerization, as reported to be a typical property of uracil-annulated heteroazulenyl cations.<sup>7–10</sup> The  $pK_{R+}$  values of **11a–c** are larger than that of **2a**; however, the first reduction potentials ( $E1_{red}$ ) of **11a–c** are more positive than that of **2a**. This feature is rationalized by the elongated  $\pi$ -conjugation of **11a–c** as compared with **2a–c**.

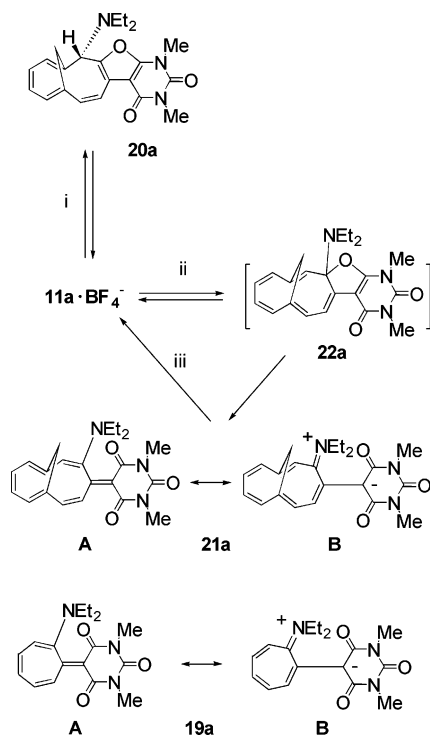
**Reactivity of 11a.** The reaction site of **2a**· $BF_4^-$  and **3a–c**· $BF_4^-$  with some nucleophiles depends on the nucleophiles and heteroatom on the cations.<sup>8–10</sup> Thus, the reactions of **11a**· $BF_4^-$  with some nucleophiles were carried out. Reduction of **11a**· $BF_4^-$  with NaBH<sub>4</sub> in CH<sub>3</sub>CN afforded compound **17a** in good yield (Scheme 3). Compound **17a** is oxidized by DDQ to regenerate **11a**· $BF_4^-$  in good yield. Previously, we have reported that the reaction of **2a**· $BF_4^-$  or **3a–c**· $BF_4^-$  with NaBH<sub>4</sub> proceeded at the 1-, 3-, and 5-positions to afford a mixture of three regio-isomers.<sup>8–10</sup> On the other hand, the reaction of **11a**· $BF_4^-$  proceeded at only the 9-position to afford single isomer **17a**, and other regioisomers, such as **18a**, are not obtained. There is a well-known tendency for double bond fixation in the methano[11]annulene system to favor a cycloheptatriene system in the compound **17a** predominantly over a 1,6-dimethylenecyclohepta-2,4-diene system in compound **18a**.<sup>27</sup> Thus, the reaction of **11a**· $BF_4^-$  with NaBH<sub>4</sub> would occur at the 9-position. To clarify the selectivity of endo-addition or exo-addition, a reaction of **11a**· $BF_4^-$  with NaBD<sub>4</sub> was also carried out to give only endo-adduct **17a–D** selectively. This result shows that the methano[11]annulene system is useful for

(27) (a) Paquette, L. A.; Berk, H. C.; Ley, S. V. *J. Org. Chem.* **1975**, *40*, 902 and references therein. (b) Reisdorf, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 218.



**FIGURE 7.** Chemical shifts (bold) and coupling constants of **17a**.

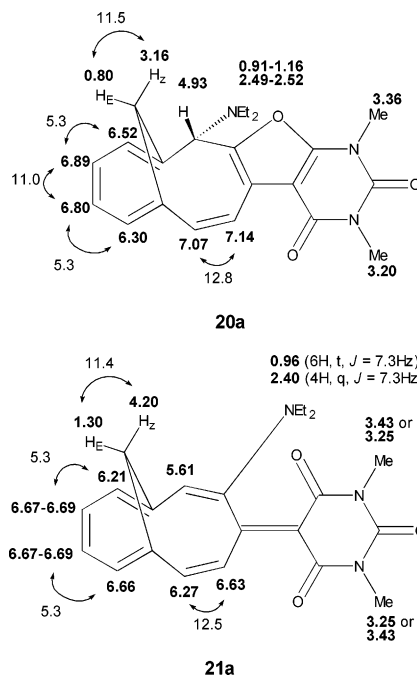
**SCHEME 4<sup>a</sup>**



<sup>a</sup> Reagents and conditions: (i) Et<sub>2</sub>NH, CD<sub>3</sub>CN, -65 °C, 30 s; (ii) warm to rt, 1h; (iii) 42% aq HBF<sub>4</sub>, Ac<sub>2</sub>O, 0 °C, 1 h.

the chiral auxiliary. Preferential endo-selectivity of nucleophiles toward **11a** is probably due to the bridge methylene, which experiences appreciable steric hindrance with the incorporating nucleophiles. The structural assignment of **17a** and **17a-D** was based on the NMR, IR and mass spectral data. The <sup>1</sup>H NMR spectra are assigned by using H–H COSY and NOE spectra, and the chemical shifts and coupling constants of **17a** are shown in Figure 7.

The reaction of **2a·BF<sub>4</sub><sup>-</sup>** with diethylamine gives 5a-adduct, which undergoes ring-opening reaction to give **19a** (Scheme 4).<sup>8</sup> Thus, the reaction of **11a·BF<sub>4</sub><sup>-</sup>** with diethylamine was monitored by NMR spectroscopy in CD<sub>3</sub>CN. Initially, diethylamine addition of **11a·BF<sub>4</sub><sup>-</sup>** occurred at the 9-position under low temperature (-65 °C) to afford **20a** (Scheme 4). The structural assignment of **20a** was based on the <sup>1</sup>H and <sup>13</sup>C NMR, although the <sup>13</sup>C NMR spectrum of **20a** shows more than eight signals of sp<sup>3</sup>-carbon, which are contaminated with some signals



**FIGURE 8.** Chemical shifts (bold) and coupling constants of **20a** and **21a**.

of Et<sub>2</sub>NH<sub>2</sub>·BF<sub>4</sub><sup>-</sup> and/or Et<sub>2</sub>NH (cf. Supporting Information). The <sup>1</sup>H NMR spectrum of **20a** is unequivocally assigned by using the H–H COSY and NOE spectra, and the chemical shifts and coupling constants are shown in Figure 8. In the NOE spectrum of **20a**, correlation between the H-9 and the H-z is suggested, and thus, the endo-orientation of the diethylamino group is assessed. This feature shows also that the methano[11]annulene system is useful for the chiral auxiliary. While the 9-adduct **20a** was stable at low temperature (-65 to -35 °C for 1 h), isomerization reaction was observed at higher temperature (>-35 °C) to give **21a** (Scheme 4). The rearrangement would proceed via 9a-adduct **22a**. Although compound **21a** is stable in dilute solution, it decomposes during concentration in vacuo. Thus, the optical resolution based on the generation of diastereomers by addition reaction of **11a·BF<sub>4</sub><sup>-</sup>** with chiral amines seems to be difficult. Satisfactory <sup>1</sup>H and <sup>13</sup>C NMR and HRMS spectra were obtained for **21a**. Based on the study of <sup>1</sup>H and <sup>13</sup>C NMR, we have reported that compound **19a** has a larger contribution of the canonical structure **19a-B**.<sup>8</sup> On the contrary, large coupling constant between the H-10' and the H-11' as well as small coupling constants between the H-5' and the H-6' and between the H-7' and the H-8' suggest that compound **21a** has a larger contribution of the canonical structure **21a-A** probably due to the stability of the cycloheptatriene-moiety.<sup>27</sup>

**Autorecycling Oxidation of Alcohols and Amines.** Compounds **2a·BF<sub>4</sub><sup>-</sup>** and **3a-c·BF<sub>4</sub><sup>-</sup>** undergo autorecycling oxidation toward some alcohols under photoirradiation.<sup>8-10</sup> In this context and in a search for oxidizing ability of **11a·BF<sub>4</sub><sup>-</sup>**, we examined the oxidation of some alcohols and amines by using **11a·BF<sub>4</sub><sup>-</sup>** under aerobic and photoirradiation conditions (RPR-100, 350 nm lamps). Although alcohols and cyclohexylamine were not oxidized by **11a·BF<sub>4</sub><sup>-</sup>**, we found that compound **11a·BF<sub>4</sub><sup>-</sup>** has oxidizing ability toward benzylamine and 1-phenylethy-

**TABLE 4. Autorecycling Oxidation of Some Alcohols and Some Amines by  $11a \cdot BF_4^-$  under Photoirradiation<sup>a</sup>**

entry	additive	alcohol or amine	carbonyl compd <sup>b</sup>	yield <sup>c</sup> /%
1	$11a \cdot BF_4^-$	PhCH <sub>2</sub> NH <sub>2</sub>	PhCHO	3007
2	$11a \cdot BF_4^-$	PhCH(NH <sub>2</sub> )Me	PhCOMe	2267
3	$11a \cdot BF_4^-$	cyclohexylamine	cyclohexanone	0 <sup>e</sup>
4	$11a \cdot BF_4^-$	PhCH <sub>2</sub> OH <sup>d</sup>	PhCHO	0 <sup>e</sup>
5	$11a \cdot BF_4^-$	PhCH(OH)Me	PhCOMe	0 <sup>e</sup>
6	$2a \cdot BF_4^-$ <sup>f</sup>	PhCH(OH)Me	PhCOMe	1860

<sup>a</sup> CH<sub>3</sub>CN solution was irradiated by RPR-100 350 nm lamps under aerobic conditions. <sup>b</sup> Isolated as 2,4-dinitrophenylhydrazone. <sup>c</sup> Based on  $11a \cdot BF_4^-$  used; the yield, called "blank", is subtracted from the total yield of carbonyl compound in the presence of  $11a \cdot BF_4^-$ . <sup>d</sup> In the presence of K<sub>2</sub>CO<sub>3</sub> (1 mmol). <sup>e</sup> The "blank" yield was higher than the yield in the presence of  $11a \cdot BF_4^-$ . <sup>f</sup> Reference 8.

amine to give benzaldehyde and acetophenone. The results are summarized in Table 4. Direct irradiation of the alcohols and amines in the absence of  $11a \cdot BF_4^-$  (named "blank") gives the corresponding carbonyl compounds in low to modest yields. Thus, the yields are calculated by subtraction of the "blank" yield from the yield of the carbonyl compound in the presence of  $2a \cdot BF_4^-$  and  $11a \cdot BF_4^-$ . More than 100% yields are obtained [based on compounds  $11a \cdot BF_4^-$ ] (Table 4, entries 1 and 2), and thus, autorecycling oxidation clearly proceeds. In a search for the mechanistic aspect of the photoinduced oxidation reaction, the fluorescence spectra of  $2a \cdot BF_4^-$  and  $3a \cdot BF_4^-$  are studied.<sup>8,9</sup> The fluorescence of **2a** and **3a** are 491 and 500 nm, and the storks-shifts are 94 and 86 nm, respectively.<sup>8,9</sup> The quantum yields ( $\Phi$ ) for **2a** and **3a** are 0.087 and 0.054, respectively, as determined by using quinine bisulfate as standard.<sup>28</sup> By addition of 1-phenylethanol to the solutions of **2a** or **3a**, quenching of the fluorescence was observed, suggesting interaction of the singlet excited state of **2a** or **3a** with the alcohol. On the other hand, the fluorescence of **11a** appeared at 531 nm, and the storks-shift was 38 nm. The fluorescence of **11a** is very weak, and the quantum yield ( $\Phi$ ) of **11a** was determined to be 0.00394 by using quinine bisulfate as standard.<sup>28</sup> In addition, by addition of 1-phenylethanol (500 equiv) to the solution of **11a** (under similar conditions for oxidation reaction), no quenching of the fluorescence was observed. These features suggest very small interaction of the singlet excited state of **11a** with alcohol, and thus, alcohols would not be oxidized by  $11a \cdot BF_4^-$ . On the other hand, the present autorecycling oxidation of amines would proceed via addition products, similar to the lumiflavinium ions.<sup>29</sup> However, attempted detection of the intermediate such as an addition product or reduced compound **17a** in the oxidation reaction was unsuccessful at the present stage. Thus, further investigations are required to clarify the present autorecycling oxidation reaction.

## Summary

The synthesis of novel 4,9-methanoundecafulvene [5-(4,9-methanocycloundeca-2',4',6',8',10'-pentaenyl-

dene)pyrimidine-2(1*H*),4(3*H*),6(5*H*)-trione] derivatives **10a–c** was accomplished. On the basis of the UV–vis and <sup>13</sup>C and <sup>1</sup>H NMR spectra, the structural characteristics and electrochemical properties were investigated. Upon oxidative cyclization with DDQ, **10a–c** were converted to 11,13-disubstituted 3,8-methanocycloundeca-[8,9-*b*]pyrimido[5,4-*d*]furan-12(11*H*),14(13*H*)-dionylum tetrafluoroborates  $11a–c \cdot BF_4^-$  in good yields. The spectroscopic properties were studied, and structural characterization of  $11b \cdot BF_4^-$  based on the X-ray crystal analysis was also performed. Due to the elongated  $\pi$ -conjugation, the  $pK_{R+}$  values of **11a–c** are remarkably larger than that of **2a**, while the first reduction potentials ( $E1_{red}$ ) of **11a–c** are more positive than that of **2a**. In the reactions of  $11a \cdot BF_4^-$  with some nucleophiles, hydride and diethylamine, the methano-bridge is proposed for a useful chiral auxiliary. Although some alcohols and cyclohexylamine were not oxidized by  $11a \cdot BF_4^-$ , the photoinduced oxidation reactions of  $11a \cdot BF_4^-$  toward some amines under aerobic conditions were carried out to give the corresponding carbonyl compounds in more than 100% yields. On the basis of the present study, uracil-annulated methano-bridged aromatic compounds, such as  $11a \cdot BF_4^-$ , are expected to provide chiral redox systems. Further studies concerning this aspect will be continued.

## Experimental Section

General experimental conditions and spectroscopic instrumentation used are described in the Supporting Information.

**General Procedure for the Preparation of 10a–c.** A solution of each of barbituric acid **9a** (624 mg, 4 mmol), **9b** (736 mg, 4 mmol), and **9c** (1120 mg, 4 mmol) and 4,9-methano-[1]annulenone **8** (170 mg, 1 mmol) in Ac<sub>2</sub>O (2 mL) was heated at 120 °C for 1.5 h. After the reaction was completed, the reaction mixture was concentrated in vacuo. The resulting residue was purified through column chromatography on Al<sub>2</sub>O<sub>3</sub> by using hexane–AcOEt (2:1) as the eluent to give the products **10a** (248 mg, 81%), **10b** (177 mg, 53%), or **10c** (286 mg, 66%).

**General Procedure for the Preparation of Salts 11a–c·BF<sub>4</sub><sup>-</sup>.** To a stirred solution of each **10a** (64 mg, 0.2 mmol), **10b** (68 mg, 0.2 mmol), and **10c** (86 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added DDQ (91 mg, 0.4 mmol), and the mixture was stirred at rt for 1 h until the reaction was completed. After evaporation of the CH<sub>2</sub>Cl<sub>2</sub>, the residue was dissolved in Ac<sub>2</sub>O (5 mL) and 42% HBF<sub>4</sub> (1 mL) at 0 °C, and the mixture was stirred for 1 h. To the mixture was added Et<sub>2</sub>O (100 mL), and the precipitates were collected by filtration to give  $11a \cdot BF_4^-$  (86 mg, 100%),  $11b \cdot BF_4^-$  (80 mg, 94%), or  $11c \cdot BF_4^-$  (110 mg, 100%).

**X-ray Structure Determination of  $11b \cdot BF_4^-$ :** reddish prisms, C<sub>22</sub>H<sub>22</sub>BF<sub>4</sub>N<sub>3</sub>O<sub>3</sub>,  $M = 463.24$ , monoclinic, space group  $P2_1/c$ ,  $a = 8.844(6)$  Å,  $b = 15.79(1)$  Å,  $c = 15.418(6)$  Å,  $\beta = 98.12(2)^\circ$ ,  $V = 2131.6(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.443$  g cm<sup>-3</sup>, crystal dimensions 0.80 × 0.40 × 0.20 mm. Data were measured on a Rigaku RAXIS-RAPID radiation diffractometer with graphite-monochromated Mo K $\alpha$  radiation. A total 19 281 reflections were collected, using the  $\omega - 2\theta$  scan technique to a maximum  $2\theta$  value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using SIR92 structure analysis software,<sup>31</sup> with 320 variables and 3217 observed reflections [ $I > 3.00\sigma(I)$ ]. The non-hydrogen atoms were refined anisotropically. The weighting scheme  $w = [3.0000\sigma_c^2(F_o) + 0.0010F_o^2 + 0.5000]^{-1}$  gave satisfactory agree-

(28) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

(29) (a) Hoegy, S. E.; Mariano, P. S. *Tetrahedron* **1997**, *53*, 5027.

(b) Kim, J.; Hoegy, S. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 100. (c) Kim, J.; Bogdan, M. A.; Mariano, P. S. *J. Am. Chem. Soc.* **1993**, *115*, 10591.

(30) Ridi, M.; Aldo, G. *Gazz. Chim. Ital.* **1952**, *82*, 13.

(31) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

ment analysis. The final  $R$  and  $R_w$  values were 0.0530 and 0.0680. The maximum peak and minimum peak in the final difference map were 0.40 and  $-0.37 \text{ e}^-/\text{\AA}^3$ .

**Determination of  $pK_{R^+}$  Value of Cations **11a–c**.** Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of  $\text{KH}_2\text{PO}_4$  (0.1 M) and  $\text{NaOH}$  (0.1 M) (for pH 6.0–8.0),  $\text{Na}_2\text{B}_4\text{O}_7$  (0.025 M) and  $\text{HCl}$  (0.1 M) (for pH 8.2–9.0), and  $\text{Na}_2\text{B}_4\text{O}_7$  (0.025 M) and  $\text{NaOH}$  (0.1 M) (for 9.2–10.8) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 3–5 mg of compounds **11a–c**· $\text{BF}_4^-$  in  $\text{CH}_3\text{CN}$  (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and  $\text{CH}_3\text{CN}$  (1 mL). The UV–vis spectrum was recorded for each cation **11a–c** 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 wavelengths (488 nm for **11a**; 490 nm for **11b**; 487 nm for **11c**) of each cation **11a–c** was plotted against pH to give a classical titration curve, whose midpoint was taken as the  $pK_{R^+}$  value.

**Cyclic Voltammetry of **10a–c** and **11a–c**.** The reduction potentials of **10a–c** and **11a–c** were determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference  $\text{Ag}/\text{AgNO}_3$  electrode. Nitrogen was bubbled through an acetonitrile solution (4 mL) of each compound ( $0.5 \text{ mmol L}^{-1}$ ) and  $\text{Bu}_4\text{NClO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) to deaerate it. The measurements were made at a scan rate of  $0.1 \text{ V s}^{-1}$  and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X–Y recorder. Immediately after the measurements, ferrocene ( $0.1 \text{ mmol}$ ) ( $E_{1/2} = +0.083$ ) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard. The compounds exhibited no reversible reduction wave: each of the reduction potentials was measured through independent scan, and they are summarized in Tables 2 and 3.

**Reaction of **11a**· $\text{BF}_4^-$  with  $\text{NaBH}_4$  [and  $\text{NaBD}_4$ ].** A solution of **11a**· $\text{BF}_4^-$  ( $0.5 \text{ mmol}$ ) and  $\text{NaBH}_4$  (19 mg,  $0.5 \text{ mmol}$ ) [or  $\text{NaBD}_4$  (20 mg,  $0.5 \text{ mmol}$ )] in  $\text{CH}_3\text{CN}$  (10 mL) was stirred at rt for 1 h. To the mixture was added saturated aqueous  $\text{NH}_4\text{Cl}$  solution, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo to give **17a** (154 mg, 100%) [or **17a-D** (155 mg, 100%)].

**Oxidation of **17a**.** To a stirred solution of **17a** ( $0.5 \text{ mmol}$ ) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added DDQ (176 mg,  $0.75 \text{ mmol}$ ), and the mixture was stirred at rt for 1 h. After evaporation of the  $\text{CH}_2\text{Cl}_2$ , the residue was dissolved in a mixture of  $\text{Ac}_2\text{O}$  (5 mL) and 42%  $\text{HBF}_4$  (1 mL) at  $0^\circ\text{C}$ , and the mixture was stirred for another 1 h. To the mixture was added  $\text{Et}_2\text{O}$  (50 mL), and the precipitates were collected by filtration to give **11a**· $\text{BF}_4^-$  (179 mg, 91%).

**$^1\text{H}$  NMR Monitoring of the Reaction of **11a**· $\text{BF}_4^-$  with  $\text{Et}_2\text{NH}$ .** To a solution of compound **11a**· $\text{BF}_4^-$  ( $0.01 \text{ mmol}$ ) in  $\text{CD}_3\text{CN}$  (0.5 mL) was added at  $-65^\circ\text{C}$   $\text{Et}_2\text{NH}$  (7.3 mg,  $0.1 \text{ mmol}$ ) in an NMR tube. The NMR measurement was carried out immediately (after ca. 30 s) at  $-65^\circ\text{C}$ , and complete conversion of **11a**· $\text{BF}_4^-$  to **20a** was observed. After the reaction mixture was warmed to  $-35^\circ\text{C}$  and kept at  $-35^\circ\text{C}$  for 1 h, no change was observed. Then, the reaction mixture was warmed to rt during 1 h, and complete conversion of **20a** to **21a** was observed.

**Reaction of **21a** with  $\text{HBF}_4$ .** To a solution of **21a** ( $0.05 \text{ mmol}$ ) and  $\text{Et}_2\text{NH}$  in  $\text{CH}_3\text{CN}$ , which was prepared by the reaction of **11a**· $\text{BF}_4^-$  (20 mg,  $0.05 \text{ mmol}$ ) with  $\text{Et}_2\text{NH}$  (7.3 mg,  $0.1 \text{ mmol}$ ) in  $\text{CH}_3\text{CN}$  (20 mL), was added a mixture of  $\text{Ac}_2\text{O}$  (5 mL) and 42% aq  $\text{HBF}_4$  (1 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 1 h. To the mixture was added  $\text{Et}_2\text{O}$  (50 mL), and the precipitate was collected by filtration to give **11a**· $\text{BF}_4^-$  (20 mg, 100%).

**General Procedure of Autorecycling Oxidation of Some Alcohols and aminEs by **11a**· $\text{BF}_4^-$ .** A  $\text{CH}_3\text{CN}$  (16 mL) solution of compound **11a**· $\text{BF}_4^-$  (2.0 mg,  $0.005 \text{ mmol}$ ) and an alcohol or an amine ( $2.5 \text{ mmol}$ , 500 equiv.) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic condition for 16 h. The reaction mixture was concentrated in vacuo, and the residue was dissolved in  $\text{Et}_2\text{O}$  and filtered. The filtrate was treated with saturated 2,4-dinitrophenylhydrazine in 6%  $\text{HCl}$  to give 2,4-dinitrophenylhydrazone. The results are summarized in Table 4.

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**Supporting Information Available:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **10a–c**, **11a–c**· $\text{BF}_4^-$ , **17a**, **17a-D**, **20a**, and **21a**. HMQC and HMBC spectra of **10b** and **11a**· $\text{BF}_4^-$ . H–H COSY spectra of **10c**, **11a**· $\text{BF}_4^-$ , **20a**, and **21a**. NOE spectra of **11a**· $\text{BF}_4^-$ , **17a-D**, and **20a**. Analytical and spectroscopic data of **10a–c**, **11a–c**· $\text{BF}_4^-$ , **17a**, **17a-D**, **20a**, and **21a**. MO calculation data of **11a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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