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## Preparation, crystal structure, and spectroscopic, chemical, and electrochemical properties of (2E,4E)-1,4-di(3-guaiazulenyl)-1,3-butadiene compared with those of (E)-1,2-di(3-guaiazulenyl)ethylene

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### ABSTRACT

Wittig reaction of (E)-3-(3-guaiazulenyl)propenal (11) with (3-guaiazulenylmethyl)triphenylphosphonium bromide (9) in ethanol containing NaOEt at 25 °C for 24 h under argon gives the title new (2E,4E)-1,3-butadiene derivative 4, in 33% isolated yield, which upon treatment with hexafluorophosphoric acid (i.e., 65% HPF<sub>6</sub> aqueous solution) in tetrahydrofuran (=THF) at 25 °C for 1 h under aerobic conditions affords a new air (two-electron) oxidation product (E)-ethylene-1,2-bis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (14), quantitatively, and further, zinc-reduction of 14 in trifluoroacetic acid (=CF<sub>3</sub>COOH) at 0 °C for 1 h under argon reverts 4, quantitatively. Along with the above interesting results, our discovered another preparation method, spectroscopic properties, crystal structure, and electrochemical behavior of 4, which serves as a strong two-electron donor and acceptor, compared with those of the previously reported (E)-1,2-di(3-guaiazulenyl)ethylene (3) are documented in detail.

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### 1. Introduction

In the previous papers,<sup>1–29</sup> we reported a facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of new conjugated  $\pi$ -electron systems possessing a 3-guaiazulenyl (=5-isopropyl-3,8-dimethylazulen-1-yl)<sup>1-18,20-26,28,29</sup> [or an azulen-1-yl<sup>10,17,27</sup> or a 3-(methox-ycarbonyl)azulen-1-yl<sup>19</sup>] group. During the course of our basic and systematic investigations on parent azulene and its derivatives, in 2010 we discovered that (2E,4E)-4-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)-1,3-butadiene<sup>25</sup> (**2**), formed by the C, H, and N elements, served as a more strong two-electron donor in comparison with (*E*)-2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl) ethylene<sup>20</sup>( $\mathbf{1}$ ) and as a similar one-electron acceptor to  $\mathbf{1}$  (see Chart 1). Referring each  $\pi$ -HOMO (corresponding to ionization potential) and  $\pi$ -LUMO (corresponding to electron affinity) distribution diagram on the ball and stick molecular structures of 1 and 2, a redox mechanism based on the redox potentials of 2, compared with those of  $\mathbf{1}$ ,<sup>20,25</sup> by means of cyclic voltammogram (=CV) and differential pulse voltammogram (=DPV) was proposed.<sup>25</sup> In relation to studies on a preparation and characteristic properties of the conjugated  $\pi$ -electron systems **1** and **2**, for example, a preparation and anti-cancer activity of (E)-1-aryl-2-(3-guaiazulenyl)ethylenes and (2E,4E)-1-aryl-4-(3-guaiazulenyl)-1,3-butadienes have been reported<sup>30</sup> and besides, a preparation and anti-coccidial activity,<sup>31</sup> quadratic non-linear optical properties,<sup>32,33</sup> fluorescence properties,  $^{34-36}$  and functional dyes  $^{37}$  of (E)-1-aryl-2-[4-(dimethylamino) phenyl]ethylenes and (2E,4E)-1-aryl-4-[4-(dimethylamino)phenyl]-1,3-butadienes have been studied to a considerable extent; however, none have really been documented for the accurate crystal structures as well as the detailed spectroscopic, chemical, and electrochemical properties of those compounds. Along with the above basic studies,<sup>1–37</sup> our next challenge has quite recently been focused on the following investigations: namely, (i) preparation, crystal structure, and characteristic properties of the title new



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**Chart 1.** The structures and of conjugated  $\pi$ -electron systems 1–4.

extended  $\pi$ -electron system **4** compared with those of the previously reported (*E*)-1,2-di(3-guaiazulenyl)ethylene<sup>10</sup> (**3**) (see Chart 1). Especially, the target non-benzenoid aromatic compound **4**, formed by the C and H elements, can be expected to serve as a more strong two-electron donor and acceptor in comparison with **3**, the phenomena, of which are noteworthy as an organic and electronic material; and (ii) study on a plausible redox mechanism based on the CV and DPV data of **4**, compared with those of **3**, along with their MO calculations. We now wish to report the detailed studies on the above (i) and (ii) together with some other specific experimental results.

#### 2. Results and discussion

# 2.1. Preparation and spectroscopic properties of 4 compared with those of 3

In 1984 (*E*)-1,2-di(3-guaiazulenyl)ethylene (**3**) (see Chart 1) was prepared, in 72% yield, by using the McMurry reaction of guaiazulene-3-carbaldehyde (**8**) and further, the UV–vis and <sup>1</sup>H NMR spectroscopic and electrochemical properties of **3** were reported.<sup>38–40</sup> In relation to the above studies, in 2004 we reported the crystal structure and the spectroscopic, chemical, and electrochemical properties as well as our discovered preparation method of **3**,<sup>10</sup> the compound, of which was prepared according to Scheme 1: namely, the reaction of a naturally occurring guaiazulene (**6**) with glyoxal (**5**) in acetic acid containing 42% tetrafluoroboric acid at 25 °C for 1 h gave  $\alpha, \alpha'$ -bis(3-guaiazulenylmethylium) bis(tetra-fluoroborate) (**7**), in 98% isolated yield, which upon Zn-reduction in trifluoroacetic acid at 0 °C for 5 min under argon afforded **3** in 94% isolated yield. As comparative studies on the characteristic properties of **4** with those of **3**, the guaiazulene dimmer **4** connected with a (2E,4E)-1,3-butadiene linkage was prepared, in 33% isolated yield, by using the Wittig reaction of (E)-2-(3-guaiazulenyl)ethylene-1-carbaldehyde (**11**) with (3-guaiazulenylmethyl)triphenylphosphonium bromide (**9**) shown in Scheme 2 and Sections 4.1.1–4.1.3. The molecular structure of **4** was established on the basis of spectroscopic data [UV–vis, exact FABMS, and <sup>1</sup>H and <sup>13</sup>C NMR including 2D NMR (i.e., DQF COSY, HSQC, and HMBC)].

Besides the preparation method of **4** shown in Scheme 2, similar to Scheme 1, the target compound **4** was prepared according to our discovered procedures shown in Scheme 3 and Sections 4.1.4–4.1.6: namely, the reaction of **6** with ethylene-1,2-dicarbaldehyde (**13**), derived from the MnO<sub>2</sub>-oxidation of (2*Z*)-2-butene-1,4-diol (**12**) (see Section 4.1.4), in a mixed solvent of acetonitrile and diethyl ether containing 65% hexafluorophosphoric acid at 25 °C for 1 h gave a new (*E*)-ethylene-1,2-bis(3-guaiazulenylmethylium) bis(h-exafluorophosphate) (**14**), in 13% isolated yield, which upon Zn-reduction in trifluoroacetic acid at 0 °C for 1 h under argon afforded **4** in 98% isolated yield. The structure of **14** was established on the basis of elemental analysis (=EA) and spectroscopic data [UV–vis, IR, exact FABMS, and <sup>1</sup>H and <sup>13</sup>C NMR including 2D NMR (i.e., DQF COSY, HSQC, and HMBC)].

The title compound 4 was obtained as dark-green needles, while a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub> was dark-yellow. The spectroscopic properties of **4** compared with those of  $3^{10}$  are described as follows: namely, the UV-vis spectrum of **4** showed that the characteristic absorption bands based on the starting material guaiazulene<sup>41</sup> ( $\mathbf{6}$ ) were not observed, indicating the formation of the molecular structure **4** with an extended  $\pi$ -electron system between the guaiazulene dimmer 4 connected with a (2E,4E)-1,3-butadiene linkage; the spectral pattern of **4** resembled that of **3** (see Fig. 1), while a characteristic absorption wavelength ( $\lambda_{max}$  473 nm, log  $\epsilon$ =4.77) of **4** showed a bathochromic shift ( $\Delta$ 14 nm) and a hyperchromic effect ( $\Delta \log \epsilon = 0.22$ ) in comparison with the corresponding wavelength ( $\lambda_{max}$  459 nm, log  $\epsilon$ =4.55) of **3**, the results, of which supported the difference between the  $\Delta\pi$ -HOMO $-\pi$ -LUMO (-6.137 eV) of **4** (see Section 2.5) and that (-6.282 eV) of **3**;<sup>20</sup> however, the longest absorption wavelength ( $\lambda_{max}$  647 nm, log  $\epsilon$ =3.20) of **4** revealed a hypsochromic shift ( $\Delta$ 32 nm) and a hyperchromic effect ( $\Delta \log \epsilon = 0.13$ ) in comparison with that ( $\lambda_{max}$  679 nm, log  $\epsilon$ =3.07) of **3**, presumably owing to a solvent effect.<sup>42</sup> The molecular formula C34H38 was determined by exact FABMS, the spectrum, of which showed the M<sup>+</sup> ion peak. The <sup>1</sup>H NMR spectrum showed signals from an equivalent of two 3-guaiazulenyl groups and signals based on a (2E,4E)-1,3-butadiene unit possessing an equivalent of two substituents at the C-1 and C-4 positions, all the signals, of which were carefully assigned using computer-assisted simulation based on first-order analysis and DQF COSY. As the results, an equivalent of the two 3-guaiazulenyl proton signals of 4 except an equivalent of the H-2',2" proton signals coincided with those of 3; however, an equivalent of the H-2',2" proton signals of 3



Scheme 1. An efficient preparation of 3 by using the Zn-reduction of 7 obtained from the reaction of 6 with 5.





Scheme 3. Another preparation method of 4 by using the Zn-reduction of 14 obtained from the reaction of 6 with 13, which is derived from the MnO<sub>2</sub>-oxidation of 12.



Fig. 1. UV-vis spectra of 3 (a) and 4 (b) in CH<sub>2</sub>Cl<sub>2</sub>. Concentrations, 3: 0.10 g L<sup>-1</sup> (238  $\mu$ mol L<sup>-1</sup>), 4: 0.10 g L<sup>-1</sup> (224  $\mu$ mol L<sup>-1</sup>). Length of cell, 0.1 cm each. Each log  $\epsilon$  value is given in parenthesis.

showed a down-field shift ( $\Delta\delta$  0.15) in comparison with that of **4**; and further, an equivalent of the H-1,2 proton signals of **3** revealed a down-field shift ( $\Delta\delta$  0.38) in comparison with an equivalent of the H-1,4 proton signals of **4**, owing to the difference between an influence of a ring current generated from the guaiazulene dimmer **3** connected with an (*E*)-ethylene linkage and that generated from

the guaiazulene dimmer **4** connected with a (2*E*,4*E*)-1,3-butadiene linkage. The <sup>13</sup>C NMR spectrum exhibited 16 carbon signals assigned using HSQC and HMBC. As the results, an equivalent of the two 3-guaiazulenyl carbon signals of **4** coincided with that of **3**, while an equivalent of the two C-1,4 carbon signals of **4** showed a down-field shift ( $\Delta\delta$  2.6) in comparison with an equivalent of the

two C-1,2 carbon signals of **3**, owing to the same reason described as the above <sup>1</sup>H NMR chemical shift. Thus, the total spectroscopic analyses for **4** led to the molecular structure illustrated in Chart 1.

#### 2.2. X-ray crystal structure of 4 compared with that of 3

The recrystallization of **3** from a mixed solvent of hexane and dichloromethane (5:1, vol/vol) provided single crystals suitable for X-ray crystallographic analysis, the recrystallization conditions, of which were the same as our previous paper.<sup>10</sup> The crystal structure of **3** was then determined by means of X-ray diffraction (see Section 4.1.10), supporting the C–C bond alternation pattern of **3** illustrated in Chart 1, the obtained accurate structural parameters, of which were better than those reported in our previous paper.<sup>10</sup> The ORTEP drawing of **3** with a numbering scheme is shown in Fig. 2a together with the selected C–C bond lengths. As a specific result, it was found that the crystal structure of **3** reported in our previous paper<sup>10</sup> was planar, while the two guaiazulene rings of **3** now twisted by 19.4° from the plane of the *trans*-HC=CH– unit, respectively, presumably owing to an influence for the formation

diffraction (Section 4.1.8), supporting the C–C bond alternation pattern of **4** illustrated in Chart 1. The ORTEP drawing of **4** with a numbering scheme is shown in Fig. 3a together with the selected C-C bond lengths. As a specific result, it was found that the guaiazulene ring A and the other guaiazulene ring B twisted by 16.9° (for A) and 22.4° (for B) from the plane of the (2E,4E)-1.3butadiene unit (see Fig. 3a), presumably owing to a similar reason to 3. Thus, the molecular structure of 4 formed an antisymmetrical structure in a single crystal. Furthermore, the calculations for the crystal structure of 4 using the crystallographic software package (see Section 4.1.8) indicated that 4 generated a weak dipole moment of 0.361 debye (=D). Along with the ORTEP drawing of **4**, the crystal packing diagram of **4** revealed that those molecules formed  $\pi$ -stacking structures in the single crystal, and showed that each average inter-plane distance between overlapping molecules [i.e., the guaiazulene ring A of a molecule and the guaiazulene ring B of another molecule], which were overlapped so that those dipole moments might be negated mutually, was 3.39 Å (see Fig. 3b), the distance, of which was shorter than that (3.52 Å) of **3** (see Fig. 2b).



**Fig. 2.** (a) The ORTEP drawing (30% probability thermal ellipsoids), with a numbering scheme, of **3** (symmetrical form). The selected C–C bond lengths (Å) of **3** are as follows: C1'-C2'; 1.369(2), C2'-C3'; 1.413(2), C3'-C3a'; 1.413(2), C3a'-C4'; 1.415(2), C4'-C5'; 1.397(2), C5'-C6'; 1.403(2), C6'-C7'; 1.375(3), C7'-C8'; 1.410(2), C8'-C8a'; 1.370(2), C8a'-C1'; 1.425(2), C3a'-C8a'; 1.505(2), C3'-C1; 1.450(2), and C1-C2; 1.341(2). (b) The crystal packing diagram of **3**. Hydrogen atoms are omitted for reasons of clarity.



**Fig. 3.** (a) The ORTEP drawing (30% probability thermal ellipsoids), with a numbering scheme, of **4** (anti-symmetrical form). The selected C–C bond lengths (Å) of **4** are as follows: C1'–C2'; 1.377(3), C2'–C3'; 1.421(3), C3'–C3a'; 1.421(3), C3a'–C4'; 1.408(3), C4'–C5'; 1.401(3), C5'–C6'; 1.402(3), C6'–C7'; 1.382(3), C7'–C8'; 1.413(3), C8'–C8a'; 1.374(3), C8a'–C1'; 1.430(3), C3a'–C8a'; 1.496(3), C3'–C1; 1.459(3), C1''–C2''; 1.379(2), C2''–C3''; 1.426(3), C3'–C3a''; 1.423(3), C3a'–C4''; 1.410(3), C4''–C5''; 1.400(3), C5''–C6''; 1.395(3), C6''–C7''; 1.387(3), C7''–C8''; 1.406(2), C3''–C4'; 1.449(3), C1–C2; 1.358(3), C2–C3; 1.434(3), and C3–C4; 1.352(3). (b) The crystal packing diagram of **4**. Hydrogen atoms are omitted for reasons of clarity.

of the intermolecular  $\pi$ -stacking structures (see Fig. 2b). Thus, the crystal structure of **3** formed a symmetrical structure in a single crystal. Along with the ORTEP drawing of **3**, the average interplane distance (3.52 Å) between the over-lapping molecules of **3** (see Fig. 2b) was shorter than that (3.82 Å) reported in our previous paper.<sup>10</sup> Similar to **3**, the recrystallization of **4** from a mixed solvent of hexane and dichloromethane (5:1, vol/vol) provided single crystals suitable for X-ray crystallographic analysis. The crystal structure of **4** was also determined by means of X-ray

#### 2.3. Spectroscopic properties of 14 compared with those of 7

The dicarbenium ion compound **14** was obtained as dark-green needles, while a solution of **14** in CF<sub>3</sub>COOH was purple. The <sup>1</sup>H NMR spectra of **7**<sup>10</sup> and **14**, using a solution of CD<sub>3</sub>CN (or CD<sub>2</sub>Cl<sub>2</sub>) as a measurement solvent, showed extremely complicated signals,<sup>43</sup> which could not be assigned. However, those spectra, measured in a solution of CF<sub>3</sub>COOD, revealed all the proton signals, which could be assigned. Therefore, the UV–vis spectra of **7**<sup>10</sup> and

**14** were measured in a solution of CF<sub>3</sub>COOH. The UV–vis spectrum of **14** showed that the spectral pattern of **14** resembled that of the related dicarbenium ion compound **7**;<sup>10</sup> however, the longest absorption wavelength ( $\lambda_{max}$  561 nm, log  $\varepsilon$ =4.94) of **14** revealed a larger bathochromic shift ( $\Delta$ 37 nm) and a larger hyperchromic effect ( $\Delta$ log  $\varepsilon$ =0.28) in comparison with that ( $\lambda_{max}$  524 nm, log  $\varepsilon$ =4.66) of **7** (see Fig. 4), owing to the formation of the extended  $\pi$ -electron system **14** in comparison with the  $\pi$ -electron system **7**.

 $(\Delta \delta \ 1.99) > H-6',6'' \ (1.43) > H-1,2 \ (0.87) > (CH_3)_2CH-7',7'' \ (0.79) > H-\alpha',\alpha'' \ (0.75) > H-8',8'' \ (0.72) > Me-4',4'' \ (0.54) > (CH_3)_2CH-7',7'' \ (0.36) > H-2',2'' \ (0.08) > Me-1',1'' \ (0.07).$  Along with those <sup>1</sup>H NMR chemical shifts  $(\delta)$ , the difference between the H–H coupling constants (*J*) of **4** and those of **14** was observed as shown in Section 4.1.3 (for **4**) and Section 4.1.5 (for **14**). Moreover, all the <sup>13</sup>C NMR signals for the azulene ring and the ethylenebis(methylium) unit of **14** revealed larger down-field shifts in comparison with



Fig. 4. UV–vis spectra of 7 (a) and 14 (b) in CF<sub>3</sub>COOH. Concentrations, 7: 0.10 g L<sup>-1</sup> (168 μmol L<sup>-1</sup>), 14: 0.11 g L<sup>-1</sup> (149 μmol L<sup>-1</sup>). Length of cell, 0.1 cm each. Each log ε value is given in parenthesis.

The formula C<sub>34</sub>H<sub>38</sub> for the dicarbenium ion structure of 14 was determined by exact FABMS, the spectrum, of which showed the  $[M-2PF_6]^{2+}$  ion peak and further, an elemental analysis (=EA) of 14 confirmed the formula  $C_{34}H_{38}O_4F_{12}P_2$  (i.e.,  $C_{34}H_{38}+2PF_6+2O_2$ ). The IR spectrum of 14 showed two specific bands ( $v_{max}$  841 and 559 cm<sup>-1</sup>) based on the counter anion ( $PF_6^-$ ). The <sup>1</sup>H and <sup>13</sup>C NMR signals ( $\delta$ ) of **14** revealed signals based on an equivalent of two 3guaiazulenylmethylium ion units and on an (E)-ethylene unit possessing an equivalent of two substituents at the C-1 and C-2 positions, all the proton and carbon signals, of which were carefully assigned using similar analyses to 4. Thus, the EA and the total spectral analyses of **14** led to the dicarbenium ion structure illustrated in Scheme 3. The UV-vis spectrum of 7 (see Fig. 4a) showed that the specific absorption band ( $\lambda_{max}$  524 nm, log  $\epsilon$ =4.66) of **7** revealed a larger bathochromic shift ( $\Delta$ 65 nm) and a hyperchromic effect ( $\Delta \log \epsilon = 0.11$ ) in comparison with the corresponding absorption band ( $\lambda_{max}$  459 nm, log  $\epsilon$ =4.55) of **3** (see Fig. 1a) and further, all the <sup>1</sup>H and <sup>13</sup>C NMR signals of **7**<sup>10</sup> showed larger down-field shifts in comparison with those of **3**,<sup>10</sup> the detailed spectral analyses, of which suggested the formation of 7 with a representative resonance structure of 7a (see Chart 2). Similarly, as in the case of 7, the UV-vis spectrum of 14 (see Fig. 4b) showed that the specific absorption band ( $\lambda_{max}$  561 nm, log  $\varepsilon$ =4.94) of **14** revealed a larger bathochromic shift ( $\Delta$ 88 nm) and a hyperchromic effect ( $\Delta \log \epsilon = 0.17$ ) in comparison with the corresponding absorption band ( $\lambda_{max}$  473 nm, log  $\epsilon$ =4.77) of **4** (see Fig. 1b). Furthermore, all the <sup>1</sup>H NMR signals of **14** showed apparently down-field shifts in comparison with those of 4 (see Table 1): namely, the order of a larger down-field shift was H-5',5"



Chart 2. 7 with a representative resonance structure of 7a.

those of **4** (see Table 2): namely, the order of a larger down-field shift was C-7',7" ( $\Delta\delta$  35.4)>C-5',5" (25.2)>C-8a',8a" (23.3)>C-1',1" (22.3)>C-3a',3a" (21.6)>C-3',3" (19.1)>C- $\alpha$ , $\alpha'$  (17.8)>C-1,2 (14.8)>C-4',4" (13.1)>C-6',6" (11.7)>C-8',8" (6.9)>C-2',2" (3.4). Thus, the detailed spectral analyses suggested the formation of **14** with the representative three resonance structures of **14a**–**c** (see Chart 3).

# 2.4. X-ray crystal structure of 14 compared with those of 7 and 4

In 2004 we reported an efficient preparation and spectroscopic and chemical properties of  $\alpha, \alpha'$ -bis(3-guaiazulenylmethylium)  $bis(tetrafluoroborate)^{10}(7)$ ; however, its crystal structure could not be elucidated. Recently, we discovered that the recrystallization of 7 from a mixed solvent of diethyl ether and acetonitrile (5:1, vol/vol) provided stable single crystals suitable for X-ray crystallographic analysis. The crystal structure of 7 was then determined by means of X-ray diffraction, the accurate structural parameters (see Section 4.1.11), of which supported the C–C bond alternation pattern of a resonance structure 7a illustrated in Chart 2. As a specific result, the plane of the 3-guaiazulenylmetylium ion unit of 7 twisted by 17.5° from that of the other 3-guaiazulenvlmetvlium ion unit. owing to the influence of the steric hindrance and repulsion and the electrostatic repulsion between an equivalent of the two 3-guaiazulenylmethylium ion units. Along with the ORTEP drawing of 7 (see Fig. 5a), the crystal packing diagram of 7 revealed that the compound formed  $\pi$ -stacking structure in the single crystal, and showed that each average inter-plane distance between overlapping structures (i.e., the seven-membered ring of a structure and the two methylium ion units of another structure), which were overlapped obliquely so that both of the electrostatic repulsion might be evaded mutually, was 3.46 Å (see Fig. 5b). Similar to 7, the recrystallization of 14 from a mixed solvent of diethyl ether and acetonitrile (5:1, vol/vol) provided stable single crystals suitable for X-ray crystallographic analysis. The crystal structure of 14 was also determined by means of X-ray diffraction, the accurate structural parameters (see Section 4.1.9), of which supported the C-C bond alternation pattern of a resonance structure 14c illustrated in Chart 3. As a specific result, compound 7 was not planer; however,

Table 1	
<sup>1</sup> H NMR signals ( $\delta$ ) of <b>4</b> in benzene- $d_6$ compared with those of <b>14</b> in CF <sub>3</sub> COOD	

Compound	3-Guaiazulenyl group									
	(CH <sub>3</sub> ) <sub>2</sub> CH-7',7"	Me-1',1"	Me-4',4"	(CH <sub>3</sub> ) <sub>2</sub> CH-7',7"	H-2′,2″	H-6′,6″	H-5′,5″	H-8′,8″		
4	1.19	2.53	2.87	2.71	7.99	6.97	6.55	7.92		
14	1.55	2.60	3.41	3.50	8.07	8.40	8.54	8.64		
Compound				Butadiene unit						
				H-1,4				H-2,3		
4				7.74				7.20		
Compound				Ethylenebis(methylium) unit						
				H-1,2				Η-α',α″		
14				8.07				8.49		

Table 2

The selected <sup>13</sup> C NMR signals ( $\delta$ )	of <b>4</b> in benzene-d <sub>6</sub> compared with	those of 14 in CF <sub>3</sub> COOD
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Compound	nd Azulene ring									
	C-1′,1″	C-2′,2″	C-3′,3″	C-3a',3a″	C-4',4"	C-5′,5″	C-6′,6″	C-7′,7″	C-8′,8″	C-8a',8a″
4	126.6	136.3	128.0	132.7	146.4	127.3	134.7	140.6	133.4	141.8
14	148.9	139.7	147.1	154.3	159.5	152.5	146.4	176.0	140.3	165.1
Compound					Butadiene unit					
					C-1,4					C-2,3
4					127.8					130.0
Compound					Ethylenebis(methylium) unit					
					C-1,2					C-α,α'
14					144.8					145.6





Chart 3. 14 with the representative three resonance structures of 14a-c.

compound **14** was planer, presumably owing to the formation of a resonance structure **14c**. Along with the ORTEP drawing of **14** (see Fig. 6a), the crystal packing diagram of **14** revealed that the compound formed  $\pi$ -stacking structure in the single crystal, and showed that each average inter-plane distance between overlapping structures [i.e., the seven-membered ring of a structure and the (*E*)-ethylene unit of another structure], which were overlapped obliquely so that both of the electrostatic repulsion might be evaded mutually, was 3.61 Å (see Fig. 6b), whose distance was longer than that (3.46 Å) of **7**, presumably owing to the difference between the resonance formations and the counter ion of **14** and those of **7**. For comparative purposes, the selected C–C bond lengths (Å) of **4** compared with those of **14** are shown in Table 3, supporting each C–C bond alternation pattern based on the molecular structure **4** and a resonance structure **14c** illustrated in Charts 1 and 3.

#### 2.5. Electrochemical behavior of 4 compared with that of 3

We have been interested further in a comparative study of the electrochemical property of 4 with that of 3. The electrochemical behavior of 3 was measured by means of CV (=Cyclic voltammogram) and DPV (=Differential pulse voltammogram) [Potential (in volt) versus SCE] in CH<sub>3</sub>CN containing 0.1 M [n-Bu<sub>4</sub>N]BF<sub>4</sub> (see Fig. 7a,b). As the results, four redox potentials observed by DPV were positioned at the  $E_p$  values of +0.39, +0.24, -1.67, and -1.86 V and further, the corresponding four reversible redox potentials  $(E_{1/2})$ determined by CV were located at the values of +0.37, +0.22, -1.70, and -1.87 V. However, the electrochemical behavior of 4 could not be measured under the same measurement conditions as for 3, because the dark-brown polar resinous substances were precipitated, quantitatively, as soon as we measured, while the CV and DPV of 4 could be measured in a solution of CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M [*n*-Bu<sub>4</sub>N]PF<sub>6</sub>, the measurement conditions, of which were shown in Fig. 7e,f caption. For comparative purposes, the CV and DPV of 3 were measured under the same measurement conditions as for 4. As the results, four redox potentials observed by the DPV of 3 were positioned at the  $E_p$  values of +0.42, +0.16, -1.78, and -1.98 V, and further, the corresponding two reversible oxidation potentials  $(E_{1/2})$ and two irreversible reduction potentials  $(E_{pc})$  determined by the CV of 3 were shown in Fig. 7d,c. Similar to 3, four redox potentials observed by the DPV of **4** were positioned at the  $E_p$  values of +0.25, +0.16, -1.75, and -1.89 V, and the corresponding two reversible oxidation potentials  $(E_{1/2})$  and two irreversible reduction potentials  $(E_{pc})$  were determined by the CV of **4** were shown in Fig. 7e,f, the results, of which indicated that the first redox potentials ( $E_1^{red}$  and  $E_1^{\text{ox}}$ ) of **4** coincided with those of **3**, while the second redox potentials ( $E_2^{\text{red}}$  and  $E_2^{\text{ox}}$ ) of **4** were lower than those of **3**. In conclusion, we now clarified that 4 served as a more strong two-



**Fig. 5.** (a) The ORTEP drawing (30% probability thermal ellipsoids), with a numbering scheme, of **7**. The selected C–C bond lengths (Å) of **7** are as follows: C1–C2; 1.331(3), C2–C3; 1.465(3), C3–C3a; 1.484(4), C3a–C4; 1.394(4), C4–C5; 1.408(4), C5–C6; 1.382(3), C6–C7; 1.394(3), C7–C8; 1.388(4), C8–C8a; 1.388(4), C8a–C1; 1.467(4), C3a–C8a; 1.443(3), C3–Ca; 1.371(3), and C $\alpha$ –C $\alpha$ '; 1.436(4). Compound **7** is a symmetrical structure and thus, a counter ion (BF<sub>4</sub><sup>-</sup>) is omitted. (b) The crystal packing diagram of **7**.



**Fig. 6.** (a) The ORTEP drawing (30% probability thermal ellipsoids), with a numbering scheme, of **14**. The C–C selected bond lengths (Å) of **14** are as follows: C1'–C2'; 1.3464(2), C2'–C3'; 1.4506(2), C3'–C3a'; 1.4773(2), C3a'–C4'; 1.4046(3), C4'–C5'; 1.4223(2), C5'–C6'; 1.3815(2), C6'–C7'; 1.4046(2), C7'–C8'; 1.3839(2), C8'–C8a'; 1.3896(2), C8a'–C1'; 1.4562(3), C3a'–C8a'; 1.4430(2), C3'–Ca; 1.3579(2), Ca–C1; 1.4263(2), and C1–C2; 1.358(4). Similar to **7**, compound **14** is a symmetrical structure and thus, a counter ion ( $PF_6^-$ ) is omitted. (b) The crystal packing diagram of **14**.

Та	bl	e	3

The selected C–C bond lengths (Å) of <b>4</b> compared with those of <b>1</b>	4

Atom	4	Atom	4	Atom	14
C1'-C2'	1.377(3)	C1″-C2″	1.379(2)	C1'-C2'	1.3464(2)
C2'-C3'	1.427(3)	C2"-C3"	1.426(3)	C2'-C3'	1.4506(2)
C3'-C3a'	1.421(3)	C3″-C3a″	1.423(3)	C3'-C3a'	1.4773(2)
C3a'-C4'	1.408(3)	C3a″-C4″	1.410(3)	C3a'-C4'	1.4046(3)
C4′-C5′	1.401(3)	C4″-C5″	1.400(3)	C4′-C5′	1.4223(2)
C5'-C6'	1.402(3)	C5″-C6″	1.395(3)	C5'-C6'	1.3815(2)
C6'-C7'	1.382(3)	C6″-C7″	1.387(3)	C6'-C7'	1.4046(2)
C7'-C8'	1.413(3)	C7″-C8″	1.406(2)	C7'-C8'	1.3839(2)
C8'-C8a'	1.374(3)	C8"-C8a"	1.383(2)	C8'-C8a'	1.3896(2)
C8a'-C1'	1.430(3)	C8a"-C1"	1.425(3)	C8a'-C1'	1.4562(3)
C3a'-C8a'	1.496(3)	C3a″-C8a″	1.496(2)	C3a'-C8a'	1.4430(2)
C3'-C1	1.459(3)	C3″-C4	1.449(3)	C3'-Ca	1.3579(2)
C1-C2	1.358(3)	C3–C4	1.352(3)	Ca-C1	1.4263(2)
C2-C3	1.434(3)			C1-C2	1.358(4)

electron donor and acceptor in comparison with **3**. In a previous paper,<sup>20</sup> we reported the energy levels of the  $\pi$ -HOMO (-7.372 eV),  $\pi$ -LUMO (-1.090 eV), and  $\Delta\pi$ -HOMO $-\pi$ -LUMO (-6.282 eV) for **3**. For comparative purposes, the accurate parameters for the crystal structure of **4** (see Section 4.1.8) were transferred to a SCIGRESS MO Compact V1 Pro<sup>44</sup> and then, its  $\pi$ -HOMO (corresponding to ionization potential) and  $\pi$ -LUMO (corresponding to electron affinity) energy levels were calculated, the calculation results, of which indicated the  $\pi$ -HOMO (-7.217 eV),  $\pi$ -LUMO (-1.080 eV), and  $\Delta\pi$ -HOMO $-\pi$ -LUMO (-6.137 eV). Thus, the oxidation

potentials (E/V) of **3** and **4** corresponded to their  $\pi$ -HOMO/eV energy levels and the reduction potentials (E/V) of **3** and **4** corresponded to their  $\pi$ -LUMO/eV energy levels. Referring the  $\pi$ -HOMO and  $\pi$ -LUMO distribution diagrams illustrated on the ball and stick molecular structures of 4 (see Fig. 8a,b), a redox mechanism of 4 based on DPV  $(E_p)$  datum is proposed as illustrated in Scheme 4: namely, 4 is one-electron oxidized, generating the cation-radical 4a with the resonance structure **4b**, at a potential of +0.16 V and further, **4b** is one-electron oxidized, yielding the dication 4c, at a potential of +0.25 V. Along with the oxidation potentials, 4 is one-electron reduced, generating the anion-radical 4d, at a potential of -1.75 V and further, 4d is one-electron reduced, yielding the dianion 4e, at a potential of -1.89 V. Besides, the redox potentials of the dicarbenium ion compounds 7 and 14 could not be elucidated because of difficulty in measuring those samples under the same measurement conditions as for **3** and **4** shown in Fig. 7c-f caption.<sup>45</sup>

#### 2.6. A chemical property of 4 (and 14)

In 1987 T. Nozoe et al. (S. Takekuma was one of his co-workers) reported that the autoxidation of guaiazulene (**6**) in *N*,*N*-dimethylformamide (=DMF) at 100 °C for 24 h yielded 25 separable products. A reaction pathway for the formation of those products was proposed as follows: namely, those compounds were derived, simultaneously, via the charge-transfer complex  $6^{+} \cdot O_2^{-}$  (see Chart 4) generated by the oxidation of **6** with oxygen molecule



**Fig. 7.** Cyclic and differential pulse voltammograms of **3** (3.0 mg, 7.1  $\mu$ mol) in 0.1 M [*n*-Bu<sub>4</sub>N]BF<sub>4</sub>, CH<sub>3</sub>CN (10 mL) [see (a), (b)] and **3** (3.0 mg, 7.1  $\mu$ mol) in 0.1 M [*n*-Bu<sub>4</sub>N]PF<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub> (10 mL) [see (c), (d)] and **4** (3.0 mg, 6.7  $\mu$ mol) in 0.1 M [*n*-Bu<sub>4</sub>N]PF<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub> (10 mL) [see (e), (f)] at a glassy carbon (ID: 3 mm) and a platinum wire served as working and auxiliary electrodes; scan rates 100 mV s<sup>-1</sup> at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.45 V (*E*<sub>p</sub>) by DPV and +0.42 V (*E*<sub>1/2</sub>) by CV under the same electrochemical measurement conditions as for **3** in CH<sub>3</sub>CN, and revealed +0.42 V (*E*<sub>p</sub>) by DPV and +0.42 V (*E*<sub>1/2</sub>) by CV under the same electrochemical measurement conditions as for **3** and **4** in CH<sub>2</sub>Cl<sub>2</sub>.



**Fig. 8.** The  $\pi$ -HOMO and  $\pi$ -LUMO energy levels (eV) of **4** [see (a) and (b)]<sup>44</sup> and further, each distribution diagram illustrated on the ball and stick molecular structure of **4** [see (a) and (b)].<sup>44</sup>



**Scheme 4.** A proposed redox mechanism based on the DPV datum of **4** shown in Fig. 7f and on the π-HOMO and π-LUMO distribution diagrams illustrated on the ball and stick molecular structures of **4** shown in Fig. 8a,b.



**Chart 4.** The structures of the charge-transfer complexes  $6^{+} \cdot 0_2^{-}$  (and  $4^{+} \cdot 0_2^{-}$ ) generated by the oxidations of **6** (and **4**) with oxygen molecule ( ${}^{3}O_{2}$ ).

(<sup>3</sup>O<sub>2</sub>).<sup>46</sup> Because of the relatively low oxidation potential  $(E_{pa}+0.69 \text{ V vs SCE})$ ,<sup>41</sup> **6** was expected to be easily oxidized, generating the formula  $6^+ \cdot O_2^- \cdot$ , by molecular oxygen. In relation to the above study, we have quite recently discovered a unique chemical property of 4: namely, the treatment of 4 with 65% HPF<sub>6</sub> in THF at 25 °C for 1 h under aerobic conditions gave 14 in 100% isolated yield (see Scheme 5); however, 4 dissolved in a solution of THF without 65%HPF<sub>6</sub> was allowed to stand at 25 °C for 24 h under aerobic conditions, yielding numerous autoxidation products, because 4 served as a more strong two-electron donor (see Fig. 7e,f) in comparison with **6**.<sup>41</sup> Furthermore, the reaction of **4** with 65%HPF<sub>6</sub> in THF at 25 °C for 1 h under argon did not give 14. Similar to the proposed autoxidation mechanism of 6, it can be inferred that the product 14 is derived by the oxidation of 4 with oxygen molecule  $({}^{3}O_{2})$ , producing the dicarbenium ion compound  $\mathbf{4}^{2+}$  via the charge-transfer complex  $4^{+} \cdot O_2^{-} \cdot$  shown in Chart 4. Thus, compound **4** was readily converted into the air (two-electron) oxidation product 14 under the reaction conditions shown in Scheme 5. Similar to Scheme 3, the Zn-reduction of 14 in CF<sub>3</sub>COOH at 0 °C for 1 h under argon reverted 4 in 98% isolated yield (see Scheme 5).



#### 3. Conclusion

We have reported the following eight interesting points for the title basic and systematic investigations: namely, (i) the Wittig reaction of the aldehyde **11** with the reagent **9** in EtOH containing NaOEt at 25 °C for 24 h under argon gave the title new (2E,4E)-1,3-butadiene derivative **4** in 33% isolated yield; (ii) our discovered another preparation method of **4** was reported, also: namely, the reaction of guaiazulene (**6**) with ethylene-1,2-dicarbaldehyde (**13**) in a mixed solvent of acetonitrile and diethyl ether containing 65% HPF<sub>6</sub> at 25 °C for 1 h afforded the corresponding new dicarbenium ion compound **14**, in 13% isolated yield, which upon Zn-reduction in CF<sub>3</sub>COOH at 0 °C for 1 h under argon afforded **4** in 98% isolated yield; (iii) the spectroscopic data of **4** compared with those of the previously reported (*E*)-ethylene derivative **3** were documented; (iv) the crystal structure of **4** could be determined, supporting the molecular structure established on the basis of spectroscopic data,

the accurate structural parameters, of which enabled us to compare with those of **3**; (v) the crystal structure of **14** could be determined, also, supporting the dicarbenium ion structure established on the basis of elemental analysis and spectroscopic data, the accurate structural parameters, of which enabled us to compare with those of the related dicarbenium ion compound **7** and the title compound **4**; (vi) the electrochemical behavior of **4** showed that **4** served as a more strong two-electron donor and acceptor in comparison with **3**; (vii) a redox mechanism of **4** based on its redox potentials and  $\pi$ -HOMO and  $\pi$ -LUMO distribution diagrams was proposed; and (viii) the treatment of **4** with 65% HPF<sub>6</sub> in THF at 25 °C for 1 h under aerobic conditions afforded the air (two-electron) oxidation product **14**, in 100% isolated yield, which upon Zn-reduction in CF<sub>3</sub>COOH at 0 °C for 1 h under argon reverted **4**, quantitatively.

#### 4. Experimental

#### 4.1. General

Melting points were taken on a Yanagimoto MP-S3 instrument. Thermal analyses (TG and DTA) were taken on a Shimadzu DTG-50H thermal analyzer. EI (and FAB) MS spectra were taken on a JEOL The Tandem Mstation JMS-700 TKM data system. UV—vis and IR spectra were taken on a Beckman DU640 spectrophotometer and a Shimadzu FTIR-4200 Grating spectrometer. NMR spectra were recorded with a JEOL JNM-ECA500 (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C) or JNM-ECA700 (700 MHz for <sup>1</sup>H and 176 MHz for <sup>13</sup>C) cryospectrometer at 25 °C. <sup>1</sup>H NMR spectra were assigned using computerassisted simulation (software: gNMR developed by Adept Scientific plc) on a DELL Dimension 9150 personal computer with a Pentium IV processor. Cyclic and differential pulse voltammograms were measured by an ALS Model 600 electrochemical analyzer.

4.1.1. Preparation of (E)-1-cyano-2-(3-guaiazulenyl)ethylene<sup>30</sup> (**10**). To a solution of guaiazulene-3-carbaldehyde<sup>25,26</sup> (**8**) (100 mg, 0.50 mmol) in THF (3 mL) was added a solution of diethyl cyanomethylphosphonate (0.10 mL, 0.52 mmol) in THF (2 mL) with sodium hydride (83 mg, 3.5 mmol) under argon. The mixture was stirred at 25 °C for 1 h under argon. After the reaction, the reaction solution was treated with a saturated aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and then, the resulting products were extracted with diethyl ether (10 mL×3). The extract was washed with water, dried (MgSO<sub>4</sub>), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane/ethyl acetate (8:2, vol/vol) as an eluant. The crude product thus obtained was recrystallized from petroleum ether/dichloromethane (4:1, vol/vol) to provide pure **10** (121 mg, 0.49 mmol, 97% yield) as a powder.

Compound **10**: Green powder [ $R_{\rm f}$ =0.40 on silica gel TLC (solv. hexane:ethyl acetate=8:2, vol/vol)]; mp 106 °C; exact FABMS (3-nitrobenzyl alcohol matrix), found: m/z 249.1517; calcd for C<sub>18</sub>H<sub>19</sub>N: M<sup>+</sup>, m/z 249.1517; 500 MHz <sup>1</sup>H NMR (acetonitrile- $d_3$ ), signals from a 3-guaiazulenyl group:  $\delta$  1.33 (6H, d, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7'), 2.55 (3H, d, J=0.8 Hz, Me-1'), 2.98 (3H, s, Me-4'), 3.01 (1H, sept, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7'), 7.18 (1H, d, J=10.6 Hz, H-5'), 7.51 (1H, dd, J=10.6, 2.2 Hz, H-6'), 7.86 (1H, br s, H-2'), and 8.19 (1H, d, J=16.0 Hz, H-1) and 8.31 (1H, d, J=16.0 Hz, H-2).

4.1.2. Preparation of (E)-2-(3-guaiazulenyl)ethylene-1-carbaldehyde<sup>30</sup> (**11**). To a solution of **10** (50 mg, 0.2 mol) in hexane (1.5 mL) was added a hexane solution of diisobutylaluminium hydride (=DIBAL-H, 1.0 mol/L) (1.5 mL) under argon. The mixture was stirred at -10 °C for 30 min under argon and further, was stirred at 25 °C for 24 h. After the reaction, a solution of methanol (1.5 mL) and a saturated aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (3 mL) were added to the mixture and then, was stirred at 25 °C for 20 min and further, was treated using  $10\%H_2SO_4$  aqueous solution. The resulting products were extracted with diethyl ether ( $10 \text{ mL} \times 3$ ). The extract was washed with water, dried (MgSO<sub>4</sub>), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane/ethyl acetate (8:2, vol/vol) as an eluant. The crude product thus obtained was recrystallized from hexane to provide pure **11** (38 mg, 0.15 mol, 76% yield) as crystals.

Compound **11**: Dark-green plates [ $R_f$ =0.23 on silica gel TLC (solv. hexane:ethyl acetate=8:2, vol/vol)]; mp 124 °C; exact FABMS (3-nitrobenzyl alcohol matrix), found: m/z 252.1536; calcd for C<sub>18</sub>H<sub>20</sub>O: M<sup>+</sup>, m/z 252.1514; 500 MHz <sup>1</sup>H NMR (acetonitrile- $d_3$ ), signals from a 3-guaiazulenyl group:  $\delta$  1.34 (6H, d, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7'), 2.56 (3H, d, J=0.8 Hz, Me-1'), 3.07 (3H, s, Me-4'), 3.11 (1H, sept, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7'), 7.33 (1H, d, J=10.6 Hz, H-5'), 7.54 (1H, dd, J=10.6, 2.2 Hz, H-6'), 7.98 (1H, br s, H-2'), and 8.21 (1H, d, J=15.1, 7.8 Hz, H-1) and 8.48 (1H, d, J=15.1 Hz, H-2); and a signal from a formyl group:  $\delta$  9.62 (1H, d, J=7.8 Hz, CHO).

4.1.3. Preparation of (2E,4E)-1,4-di(3-guaiazulenyl)-1,3-butadiene (**4**). To a solution of **11** (76 mg, 0.30 mmol) in ethanol (3 mL) was added a solution of (3-guaiazulenylmethyl)triphenylphosphonium bromide<sup>25,26</sup> (**9**) (165 mg, 0.30 mmol) in ethanol (3 mL) with sodium ethoxide (50 mg, 1.3 mmol) under argon. The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture and then, the resulting products were extracted with dichloromethane (20 mL×3). The extract was washed with distilled water, dried (MgSO<sub>4</sub>), and evaporated in vacuo. The residue thus obtained was carefully separated by alumina column chromatography with hexane/benzene/ethyl acetate (90:5:5, vol/vol/vol) as an eluant. The crude product **4** was recrystallized from hexane/dichloromethane (5:1, vol/vol) (several times) to provide pure **4** (45 mg, 0.10 mmol, 33% yield) as crystals.

Compound 4: Dark-green needles  $[R_{f}=0.50 \text{ on silica gel TLC}]$ (solv. hexane: benzene: ethyl acetate=90: 5: 5, vol/vol/vol)]; mp 242 °C; UV-vis  $\lambda_{max}/nm$  (log  $\varepsilon$ ) in CH<sub>2</sub>Cl<sub>2</sub>, 236 (4.49), 276 (4.55), 339 (4.45), 473 (4.77), 500 sh (4.68), 647 (3.20), and 780 sh (2.91); exact FABMS (3-nitrobenzyl alcohol matrix), found: *m*/*z* 446.2971; calcd for C<sub>34</sub>H<sub>38</sub>: M<sup>+</sup>, *m*/*z* 446.2974; 700 MHz <sup>1</sup>H NMR (benzane $d_6$ ), signals from an equivalent of two 3-guaiazulenyl groups:  $\delta$  1.19 (12H, d, J=6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 2.53 (6H, s, Me-1',1"), 2.71 (2H, sept, J=6.9 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 2.87 (6H, s, Me-4',4"), 6.55 (2H, d, *I*=10.4 Hz, H-5′,5″), 6.97 (2H, dd, *I*=10.4, 2.0 Hz, H-6′,6″), 7.92 (2H, d, J=2.0 Hz, H-8',8"), and 7.99 (2H, s, H-2',2"); and signals from a (2E,4E)-1,3-butadiene unit: δ 7.20 (2H, ddd, J=15.3, 3.7, 1.3 Hz, H-2,3) and 7.74 (2H, ddd, *J*=15.3, 3.7, 1.3 Hz, H-1,4); 176 MHz <sup>13</sup>C NMR (benzene- $d_6$ ):  $\delta$  146.4 (C-4',4"), 141.8 (C-8a',8a"), 140.6 (C-7',7"), 136.3 (C-2',2"), 134.7 (C-6',6"), 133.4 (C-8',8"), 132.7 (C-3a',3a"), 130.0 (C-2,3), 127.8 (C-1,4), 128.0 (C-3',3"), 127.3 (C-5',5"), 126.6 (C-1',1"), 37.8 ((CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 28.4 (Me-4',4"), 24.4 ((CH<sub>3</sub>)<sub>2</sub>CH-7',7"), and 13.0 (Me-1',1").

4.1.4. Preparation of ethylene-1,2-dicarbaldehyde<sup>47</sup> (**13**). To a suspension of manganese dioxide (2.57 g, 30 mmol) in chloroform (7 mL) was added a solution of a commercially available (2*Z*)-2-butene-1,4-diol (**12**) (536 mg, 6.1 mmol) in chloroform. The mixture was stirred at 25 °C for 24 h. After the reaction, the used manganese dioxide was removed using a centrifugal separator. The reaction solution was evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with ethyl acetate as an eluant, the solution, of which was evaporated in vacuo to provide **13** (264 mg, 3.1 mmol, 51% yield) as a yellow paste.

Compound **13**: Yellow paste [a mixture of *E* and *Z* forms;  $R_{\rm f}$ =0.34, 0.53 on silica gel TLC (solv. ethyl acetate)]; EIMS (70 eV), *m*/

*z* 84 (M<sup>+</sup>); IR  $\nu_{max}$  (NaCl, neat) cm<sup>-1</sup>, 2920, 2851 (C–H), 1717 (CHO), and 1543 (C=C).

4.1.5. Preparation of (E)-ethylene-1,2-bis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (14). To a solution of 13 (6 mg, 0.07 mmol) in acetonitrile (2 mL) was added a solution of hexafluorophosphoric acid (i.e., 65% HPF<sub>6</sub> aqueous solution, 0.2 mL, 0.83 mmol) and then, was stirred at 25 °C for 30 min. The mixture was added to a solution of guaiazulene (**6**) (33 mg, 0.17 mmol) in diethyl ether (2 mL) and then, was stirred at 25 °C for 1 h. After the reaction, the mixture was poured into diethyl ether (10 mL), and was centrifuged at 2.6 krpm for 1 min. The thus obtained crude product was carefully washed with diethyl ether to provide pure 14 (10 mg, 0.01 mmol, 13% yield) as crystals.

Compound 14: Dark-green needles [from acetonitrile/diethyl ether (1:5, vol/vol)]; Found: C, 51.32; H, 4.42%. Calcd for C<sub>34</sub>H<sub>38</sub>O<sub>4</sub>F<sub>12</sub>P<sub>2</sub> (i.e., C<sub>34</sub>H<sub>38</sub>+2PF<sub>6</sub>+2O<sub>2</sub>): C, 51.01; H, 4.78%; UV-vis  $\lambda_{max}/nm$  (log  $\varepsilon$ ) in CF<sub>3</sub>COOH, 265 (4.62), 334 (4.37), 430 sh (4.40), 490 sh (4.66), 530 sh (4.89), and 561 (4.94); IR  $\nu_{max}$  (KBr) cm<sup>-1</sup>, 841, 559 ( $PF_6^-$ ); exact FABMS (3-nitrobenzyl alcohol matrix), found: m/z446.3000; calcd for C<sub>34</sub>H<sub>38</sub>: [M-2PF<sub>6</sub>]<sup>2+</sup>, *m*/*z* 446.2974; 500 MHz <sup>1</sup>H NMR (trifluoroacetic acid- $d_1$ ), signals based on an equivalent of two 3-guaiazulenylmethylium moieties with a delocalized  $\pi$ -electron system at δ 1.55 (12H, d, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 2.60 (6H, br s, Me-1',1"), 3.41 (6H, s, Me-4',4"), 3.50 (2H, sept, J=6.8 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 8.03 (2H, br s, H-2',2"), 8.40 (2H, dd, *J*=11.4, 1.2 Hz, H-6',6"), 8.64 (2H, d, J=1.2 Hz, H-8',8"), 8.54 (2H, d, J=11.4 Hz, H-5',5"), and 8.49 (2H, br ddd, I=3.7, 0.6, 0.3 Hz, HC<sup>+</sup>- $\alpha',\alpha''$ ); and signals based on an (*E*)-ethylene unit:  $\delta$  8.07 (2H, br ddd, *I*=15.3, 3.7, 0.6 Hz, H-1,2); 125 MHz  $^{13}$ C NMR (trifluoroacetic acid- $d_1$ ):  $\delta$  176.0 (C-7',7"), 165.1 (C-8a',8a"), 159.5 (C-4',4"), 154.3 (C-3a',3a"), 152.5 (C-5',5"), 148.9 (C-1',1"), 147.2 (C-3',3"), 146.4 (C-6',6"), 145.6 (Cα,α'), 144.8 (C-1,2), 140.3 (C-8',8"), 139.7 (C-2',2"), 42,4 ((CH<sub>3</sub>)<sub>2</sub>CH-7',7"), 29.7 (Me-4',4"), 24.4 ((CH<sub>3</sub>)<sub>2</sub>CH-7',7"), and 14.2 (Me-1',1").

4.1.6. Zinc reduction of **14**. To a solution of **14** (10 mg, 13.7  $\mu$ mol) in trifluoroacetic acid (1 mL) was added a zinc powder (58 mg, 0.89 mmol). The mixture was stirred at 0 °C for 1 h under argon. After the reaction, the used zinc powder was removed using a centrifugal separator. The reaction solution was carefully neutralized with aq NaHCO<sub>3</sub> and then, the resulting products were extracted with diethyl ether (20 mL×3). The extract was washed with water, dried (MgSO<sub>4</sub>), and evaporated in vacuo. The residue thus obtained was carefully separated by alumina column chromatography with hexane/benzene/ethyl acetate (90:5:5, vol/vol/vol) as an eluant. The crude product **4** was recrystallized from hexane/dichloromethane (5:1, vol/vol) (several times) to provide pure **4** (6 mg, 13.4  $\mu$ mol, 98% yield) as dark green needles.

The structure of the product **4** was identified by <sup>1</sup>H NMR spectral datum (see Section 4.1.3).

4.1.7. Treatment of **4** in THF containing HPF<sub>6</sub> under aerobic conditions. To a solution of **4** (10 mg, 22  $\mu$ mol) in THF (3 mL) was added a solution of haxafluorophosphoric acid (i.e., 65% HPF<sub>6</sub> aqueous solution, 0.02 mL, 83  $\mu$ mol). The mixture was stirred at 25 °C for 1 h under aerobic conditions, precipitating a dark-purple solid of **14** and then, was centrifuged at 2.6 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile/diethyl ether (1:5, vol/vol) to provide pure **14** as crystals (16 mg, 22  $\mu$ mol, 100% yield).

The structure of the product **14** was identified by  $^{1}$ H NMR spectral datum (see Section 4.1.5).

4.1.8. X-ray crystal structure of (2E,4E)-1,4-di(3-guaiazulenyl)-1,3butadiene (**4**). The X-ray measurement of the single crystal **4** was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.71075 Å) at  $-173\pm1$  °C. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on  $F^2$ . All calculations were performed using the Crystal-Structure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-764092 for compound No. **4**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for **4**:  $C_{36}H_{38}$  (FW=470.70), dark-green plate (crystal size,  $0.58 \times 0.23 \times 0.10 \text{ mm}^3$ ), monoclinic,  $P2_1/n$  (#14), a=9.722(2) Å, b=14.089(4) Å, c=18.991(5) Å,  $\beta=91.856(3)^\circ$ , V=2599.9(11) Å<sup>3</sup>, Z=4,  $D_{calcd}=1.202 \text{ g/cm}^3$ ,  $\mu$ (Mo K $\alpha$ )=0.673 cm<sup>-1</sup>, measured reflections=24,355, observed reflections=3606, no. of variables=346, R1=0.0416, wR2=0.2108, and goodness of fit indicator=0.999.

4.1.9. X-ray crystal structure of (E)-ethylene-1,2-bis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (14). The X-ray measurement of the single crystal 14 was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.71075 Å) at  $-173\pm1$  °C. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on  $F^2$ . All calculations were performed using the CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-798771 for compound No. 14.

Crystallographic data for **14**:  $C_{36}H_{38}F_{12}P_2$  (FW=736.60), darkgreen plate (crystal size:  $0.32 \times 0.06 \times 0.03$  mm<sup>3</sup>), monoclinic,  $P_{21}/$  n (#14), a=11.2180(19) Å, b=7.7834(11) Å, c=19.541(3) Å,  $\beta=102.817(5)^{\circ}$ , V=1663.7(5) Å<sup>3</sup>, Z=2,  $D_{calcd}=1.470$  g/cm<sup>3</sup>,  $\mu$ (Mo K $\alpha$ )=2.225 cm<sup>-1</sup>, measured reflections=19,332, observed reflections=4145, No. of variables=236, R1=0.0628, wR2=0.1637, and goodness of fit indicator=1.046.

4.1.10. X-ray crystal structure of (E)-1,2-di(3-guaiazulenyl)ethylene<sup>10</sup> (**3**). The X-ray measurement of the single crystal **3** was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.71075 Å) at  $-160\pm1$  °C. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on  $F^2$ . All calculations were performed using the CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-203374 for compound No. **3**.

Crystallographic data for **3**:  $C_{32}H_{36}$  (FW=420.64), dark-green plate (crystal size:  $0.80 \times 0.45 \times 0.22 \text{ mm}^3$ ), monoclinic, *C*2/c (#15), *a*=39.004(8) Å, *b*=5.1040(9) Å, *c*=12.754(3) Å, *β*=106.942(4)°, *V*=2428.8(8) Å<sup>3</sup>, *Z*=4, *D*<sub>calcd</sub>=1.150 g/cm<sup>3</sup>,  $\mu$ (Mo K $\alpha$ )=0.642 cm<sup>-1</sup>, measured reflections=10,087, observed reflections=1800, no. of variables=164, *R*1=0.0545, *wR*2=0.1292, and goodness of fit indicator=0.887.

4.1.11. X-ray crystal structure of  $\alpha, \alpha'$ -bis(3-guaiazulenylmethylium) bis(tetrafluoroborate)<sup>10</sup> (**7**). The X-ray measurement of the single

crystal **7** was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.71075 Å) at  $-160\pm1$  °C. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on  $F^2$ . All calculations were performed using the CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-763673 for compound No. **7**.

Crystallographic data for **7**:  $C_{36}H_{38}B_2F_8$  (FW=594.25), darkpurple plate (crystal size:  $0.24 \times 0.12 \times 0.08 \text{ mm}^3$ ), triclinic, *P*-1/n (#2), *a*=8.252(3) Å, *b*=8.363(3) Å, *c*=11.007(5) Å, *α*=89.634(15)°,  $\beta$ =81.822(17)°,  $\gamma$ =76.209(15)°, *V*=729.9(5) Å<sup>3</sup>, *Z*=4, *D*<sub>calcd</sub>=1.352 g/ cm<sup>3</sup>,  $\mu$ (Mo K $\alpha$ )=1.116 cm<sup>-1</sup>, measured reflections=6987, observed reflections=3340, no. of variables=209, *R*1=0.0618, *wR*2=0.1414, and goodness of fit indicator=1.071.

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- 41. Guaiazulene (**6**): UV–vis  $\lambda_{max}$ /nm (log  $\varepsilon$ ) in CH<sub>2</sub>Cl<sub>2</sub>, 244 (4.43), 291 (4.67), 304sh (4.16), 336sh (3.56), 350 (3.71), 366 (3.54), 601(2.69), 652sh (2.61), and 728sh (2.07); DPV (*E*<sub>p</sub>), +0.65, and -1.77 V; CV, +0.69 (*E*<sub>pa</sub>), and -1.77 (*E*<sub>1/2</sub>) V under the same electrochemical measurement conditions as for **3** shown in Fig. 7a,b caption.
- 42. The UV-vis spectrum of 3: λ<sub>max</sub>/nm (log ε) in CH<sub>3</sub>CN, 232 (4.58), 264 (4.62), 329 (4.60), 454(4.68), 480sh (4.59), and 661 (3.13). Thus, the longest absorption wavelength (λ<sub>max</sub> 661 nm, log ε=3.13) of 3 in CH<sub>3</sub>CN showed a hypochromic shift (Δ18 nm) and a slight hyperchromic effect (Δlog ε=0.06) in comparison with that (λ<sub>max</sub> 679 nm, log ε=3.07) of 3 in CH<sub>2</sub>CL<sub>2</sub>, owing to a solvent effect. The UV-vis (CH<sub>3</sub>CN) spectrum of 4 was not measured because of difficulty in solving a pure sample (1.0 mg) in a solution of CH<sub>3</sub>CN (07 μ).
  43. After the <sup>1</sup>H NMR spectral measurements of 7 and 14 in a solution of CD<sub>3</sub>CN (or
- 43. After the <sup>1</sup>H NMR spectral measurements of 7 and 14 in a solution of CD<sub>2</sub>CN (or CD<sub>2</sub>Cl<sub>2</sub>), the pure samples 7 and 14 were recovered, quantitatively, by recrystallization.
- 44. The accurate parameters for the crystal structure of **4** were transferred to a SCIGRESS MO Compact V1 Pro, the computer program, of which was developed by Fujitsu Ltd., Japan, and its π-HOMO-π-LUMO energy levels (eV) were calculated. A keyword (1 SCF) was used.
- The CV and DPV measurement conditions of 7 and 14 are currently under intensive investigations.
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