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Reactions of guaiazulene with thiophene-2,5-dicarbaldehyde and furan-2,5-dicarbaldehyde in methanol in the presence of hexafluorophosphoric acid: a facile preparation and properties of delocalized dicarbenium-ion compounds stabilized by two 3-guaiazulenyl groups and a thiophene (or furan) ring

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Abstract—Reaction of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h gives as high as 90% isolated yield of the delocalized dicarbenium-ion compound, 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**). Similarly, reaction of **1** with furan-2,5-dicarbaldehyde (**4**) under the same conditions as the above reaction affords the corresponding dicarbenium-ion compound, 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**5**), in 84% isolated yield. Along with a facile preparation and the spectroscopic and electrochemical properties of **3** and **5**, comparative studies on the ^{1}H and ^{13}C NMR spectral and chemical properties of **3** and **5** with those of the delocalized mono- and dicarbenium-ion compounds [i.e., (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate (**7**), (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate (**9**), α,α'-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**10**), 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**11**), and 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**12**)] are reported. Moreover, referring to the results of the X-ray crystallographic analyses of **7**, **9**, **11**, and **12**, the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5**, calculated by a WinMOPAC (version 3.0) program using PM3 as a semiempirical Hamiltonian, are described.

1. Introduction

In the previous papers,[1–13] we reported a facile preparation and the crystal structures as well as the spectroscopic, chemical, and electrochemical properties of the delocalized mono- and dicarbenium-ion compounds stabilized by the expanded π-electron systems with a 3-guaiazulenyl group. In relation to our basic studies, the synthesis, stability, spectroscopic and chemical properties, crystal structures, electrochemical behavior, and theoretical study (e.g., ab initio calculations, DFT, GIAO-NMR, and NICS) of the azulenium-,[14–16] azulenylium- (and azulenylmethylium-)[17–27] ions and the azulen-1-yl-substituted cations[17c,28–30] have been studied to a considerable extent, and a large number of the results and discussion regarding those delocalized cations have been well documented. During the course of our systematic investigations on the delocalized 3-guaiazulenyl-substituted carbenium-ion compounds derived from naturally occurring guaiazulene[31] (**1**), we have recently found (i) that the reactions of **1** with thiophene-2-carbaldehyde (**6**) and 2-furaldehyde (**8**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min gave the corresponding monocarbenium-ion compounds, (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate (**7**) and (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate (**9**) with the representative two resonance forms [i.e., the 3-guaiazulenylium- and 2-thienylium- (or 2-furylium-) ion

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Keywords: Dicarbenium-ions; Furan-2,5-dicarbaldehyde; Guaiazulene; Molecular structures; NMR studies; Properties; Thiophene-2,5-dicarbaldehyde.

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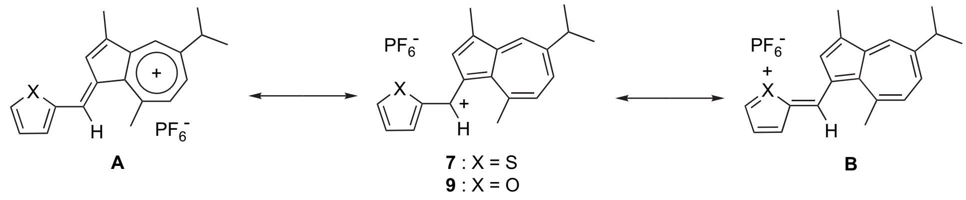
structures (**A** and **B**)] (see Chart 1), respectively, in 98 and 93% isolated yields;[10] and (ii) that the crystal structures of **7** and **9** could be determined by means of the X-ray diffraction (see Fig. 1),[10] and from the dihedral angles between the least-squares planes, it was found that the plane of the 2-thienyl group of **7** was twisted by 13.7° from the plane of the 3-guaiazulenyl group, owing to the influence of steric hindrance and repulsion between the sulfur atom of the 2-thienyl group and the H-2′ hydrogen atom of the 3-guaiazulenyl group, whose twist was larger than that between the planes of the 2-furyl and 3-guaiazulenyl groups of **9** (7.2°).[10] Moreover, from the bond lengths of **7** and **9**, it could be inferred that, although the positive charge of **7** in the single crystal was mainly localized at the C-α carbon atom, forming the 3-guaiazulenylmethylium-ion structure, the positive charge apparently was transferred to the seven-membered ring or the 2-thienyl group, forming the 3-guaiazulenylium- or 2-thienylium-ion structure and, further, the same result could be inferred for **9** (see Chart 1). As a systematic investigation on the above chemistry, our interest has quite recently been focused on a facile preparation, the molecular structures, and properties of the following dicarbenium-ion compounds, i.e., 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**) and 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**5**), with the representative four resonance forms of **C**–**F** (see Chart 2), with a view to a comparative study on those of **7** and **9**. In relation to these studies, in 2001 Ito et al. reported the synthesis, properties, and redox behavior of 2,5-thiophenediylbis[bis(3-methyl-1-azulenyl)methylium] bis(hexafluorophosphate) and 2,5-thiophenediylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate),



A

7 : X = S
9 : X = O

B

Chart 1.

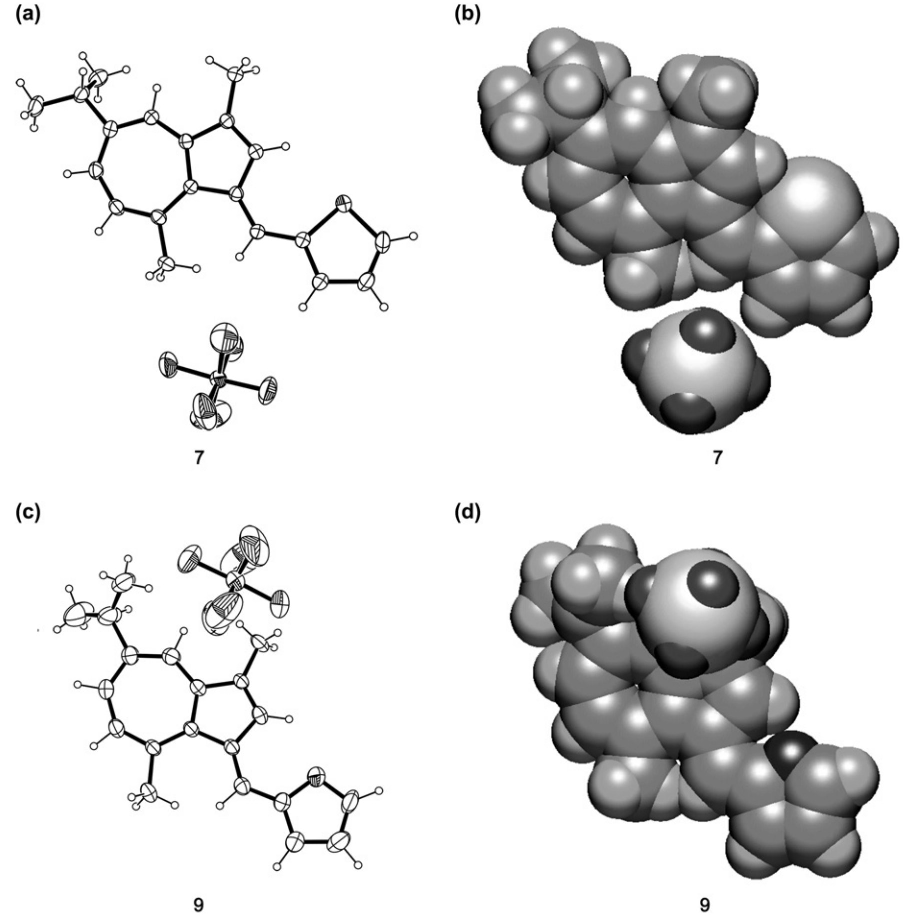


Figure 1. (a) The ORTEP drawing of **7** (30% probability thermal ellipsoids).[10] (b) The crystal structure of **7** shown using a space-filling mode. (c) The ORTEP drawing of **9** (30% probability thermal ellipsoids).[10] (d) The crystal structure of **9** shown using a space-filling mode.

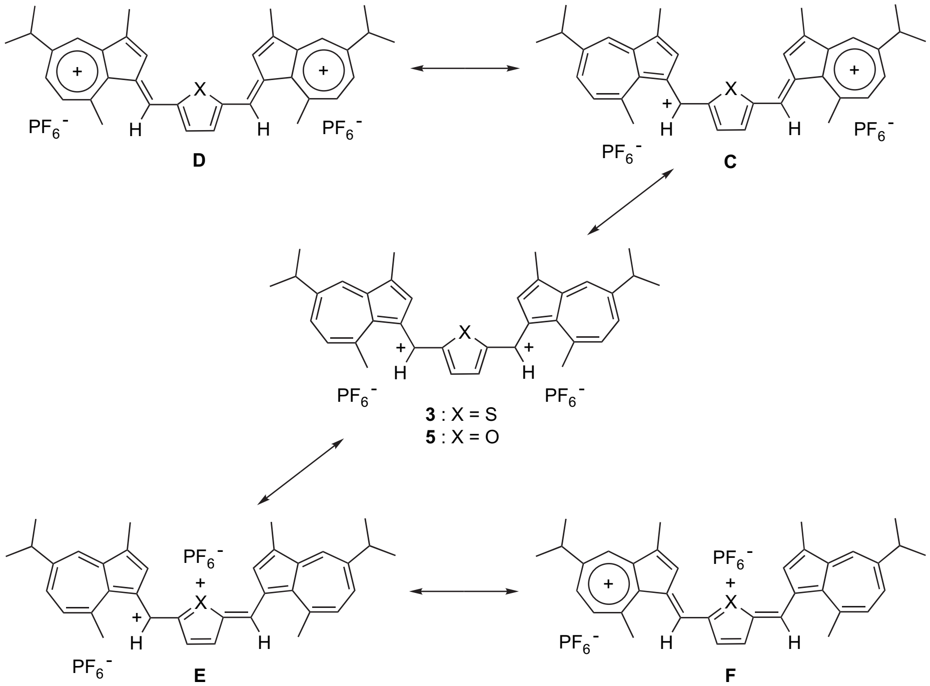


Chart 2.

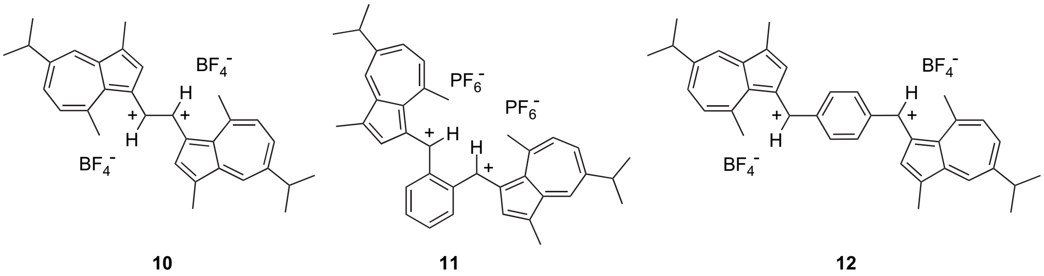
which upon reduction with zinc powder afforded the corresponding quinoid compounds, 2,5-bis[bis(3-methyl-1-azulenyl)methylene]-2,5-dihydrothiophene and 2,5-bis-[bis(3,6-di-*tert*-butyl-1-azulenyl)methylene]-2,5-dihydrothiophene, respectively.[22] We now wish to report the detailed studies on a facile preparation as well as the spectroscopic and electrochemical properties of **3** compared with those of **5** and, further, comparative studies on the ^{1}H and ^{13}C NMR spectral and chemical properties of **3** and **5** with those of the following delocalized mono- and dicarbenium-ion compounds, i.e., **7**, **9**, α,α'-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate)[8] (**10**), 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate)[4] (**11**), and 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate)[32] (**12**) (see Chart 3). Moreover, referring to the results of the X-ray crystallographic analyses of **7**, **9**, **11**, and **12**,[33] the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5**, calculated by a WinMOPAC (version 3.0) program using PM3 as a semiempirical Hamiltonian, are described,[34] because it is very difficult to obtain single crystals of **3** and **5** suitable for the X-ray crystallographic analysis.

2. Results and discussion

2.1. Preparation and properties of 2,5-thienylenebis-(3-guaiazulenylmethylium) bis(hexafluorophosphate) (3) and 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (5)

The target dicarbenium-ion compounds **3** and **5** were prepared according to the procedures shown in Figure 2 and Sections 4.1.1 and 4.1.2, whose molecular structures were established on the basis of elemental analysis and spectroscopic data [UV–vis, IR, exact FABMS, and ^{1}H and ^{13}C NMR including 2D NMR (i.e., H–H COSY, HMQC—^{1}H detected hetero nuclear multiple quantum coherence and HMBC—^{1}H detected hetero nuclear multiple bond connectivity)].

Compound **3** (90% isolated yield) was dark-green needles, mp >130 °C [decomp., determined by the thermal analysis (TGA and DTA)], while a solution of **3** in an organic solvent (e.g., CH_3CN, CH_3COCH_3, or CF_3COOH) was blue. The IR (KBr) spectrum showed two specific bands based on the



10 **11** **12**

Chart 3.

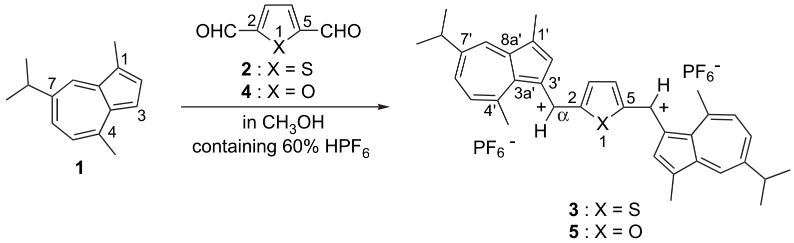


Figure 2. The reactions of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) and furan-2,5-dicarbaldehyde (**4**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h, providing the dicarbenium-ion compounds, 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**) and 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**5**), respectively.

counter anion (PF_6^-) at ν_{max} 837 and 556 cm^{-1}, which coincided with those of (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate[10] (**7**) (ν_{max} 837 and 559 cm^{-1}). The molecular formula $C_{36}H_{38}S$ for the dicarbenium-ion ($[M-2PF_6]^{2+}$) part was determined by the exact FABMS spectrum using 3-nitrobenzyl alcohol as a matrix reagent. An elemental analysis confirmed the molecular formula $C_{36}H_{38}F_{12}P_2S$. Similarly, as in the case of α,α′-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate)[8] (**10**), the 700 MHz ^1H NMR spectrum using CD_3CN as a measurement solvent showed extremely complicated signals,[35] which could not be assigned; however, that spectrum, measured in CF_3COOD, showed proton signals based on two equivalent 3-guaiazulenylmethylium-ion parts, and revealed a proton signal based on the 2,5-thienylene part, whose proton signals (δ and *J* values) were carefully assigned using the first-order analysis and the H–H COSY technique (see Table 1). The 176 MHz ^{13}C NMR (CF_3COOD) spectrum exhibited 17 carbon signals, indicating two 3-guaiazulenylmethylium substituents are equivalent, assigned by the HMQC and HMBC techniques (see Table 2). Comparative studies on the chemical shifts (δ, ppm) for the ^1H and ^{13}C NMR signals of the 3-guaiazulenylmethylium-ion part of **3** with those of **7** under the same measurement conditions are shown in Tables 1 and 2. As the results, it was found (i) that the proton signals of the H-2′ (8.34) and HC^+-α (8.81) of **3** showed slight up-field shifts in comparison with those of **7** (H-2′: 8.40 and HC^+-α: 8.91); however, the other proton signals of **3** revealed slight down-field shifts in comparison with those of **7**; namely, the order of the larger down-field shift was H-5′ (Δδ 0.14 ppm)>H-6′ (0.12)>Me_2CH-7′ (0.07)>H-8′, Me-1′, Me-4′ (0.06, each)>$(CH_3)_2CH$-7′ (0.05) (see Table 1); and (ii) that, although the carbon signals of the C-1′ (147.1), C-3′ (139.4), and C-7′ (172.8) of **3** showed down-field shifts in comparison with those of **7** (C-1′: 146.1, C-3′: 137.0, and C-7′: 171.6), the other carbon signals of **3** revealed up-field shifts in comparison with those of **7**; namely, the order of the larger up-field shift was HC^+-α (Δδ 6.5 ppm)>C-2′ (3.3)>$(CH_3)_2CH$-7′ (2.3)>Me-4′ (2.1)>C-3a′ (2.0)>C-8′, Me-1′, Me_2CH-7′ (1.8, each)>C-6′

Table 1. The ^1H NMR chemical shifts (δ, ppm) for **3**, **5**, **7**, and **9–12** in CF_3COOD at 25 °C

Compound	Me-1′	H-2′	Me-4′	H-5′	H-6′	$(CH_3)_2CH$-7′	Me_2CH-7′	H-8′	HC^+- α	H-3,4	*J*
3[a]	2.66	8.34	3.45	8.54	8.42	1.56	3.51	8.69	8.81	7.93	k
5[a]	2.74	8.65	3.48	8.57	8.45	1.60	3.55	8.73	8.44	7.67	l
Difference[b]	−0.08	−0.31	−0.03	−0.03	−0.03	−0.04	−0.04	−0.04	+0.37	+0.26	
7	2.60	8.40	3.39	8.40	8.30	1.51	3.44	8.63	8.91	7.82,[e] 7.32,[f] 8.04[g]	m
Difference[c]	+0.06	−0.06	+0.06	+0.14	+0.12	+0.05	+0.07	+0.06	−0.10		
9	2.59	8.68	3.36	8.36	8.28	1.52	3.43	8.62	8.34	7.41,[e] 6.81,[f] 7.99[g]	n
Difference[d]	+0.15	−0.03	+0.12	+0.21	+0.17	+0.08	+0.12	+0.11	+0.10		
10[a]	2.43	7.88	3.34	8.48	8.30	1.38	3.35	8.47	8.73	—	o
11[a]	2.49	7.75	3.31	8.54	8.42	1.51	3.47	8.63	8.88	7.75,[h] 7.79[i]	p
12[a]	2.58	8.03	3.47	8.59	8.44	1.55	3.51	8.68	8.85	7.98[j]	q

[a] Two 3-guaiazulenylmethylium-ion parts are equivalent.
[b] Difference of the chemical shifts for **3** and **5**.
[c] Difference of the chemical shifts for **3** and **7**.
[d] Difference of the chemical shifts for **5** and **9**.
[e] H-3.
[f] H-4.
[g] H-5.
[h] H-4,5.
[i] H-3,6.
[j] H-2,3,5,6.
[k] $J_{(CH_3)_2CH\text{-}7'}=6.9$ Hz, $J_{5',6'}=11.2$ Hz, $J_{6',8'}=2.0$ Hz.
[l] $J_{(CH_3)_2CH\text{-}7'}=6.9$ Hz, $J_{5',6'}=11.3$ Hz, $J_{6',8'}=2.2$ Hz.
[m] $J_{(CH_3)_2CH\text{-}7'}=6.9$ Hz, $J_{5',6'}=11.2$ Hz, $J_{6',8'}=2.1$ Hz, $J_{3,4}=3.9$ Hz, $J_{4,5}=5.0$ Hz.
[n] $J_{(CH_3)_2CH\text{-}7'}=6.9$ Hz, $J_{5',6'}=11.2$ Hz, $J_{6',8'}=2.0$ Hz, $J_{3,4}=3.6$ Hz, $J_{4,5}=1.4$ Hz.
[o] $J_{(CH_3)_2CH\text{-}7'}=7.0$ Hz, $J_{5',6'}=11.0$ Hz, $J_{6',8'}=2.0$ Hz.
[p] $J_{(CH_3)_2CH\text{-}7'}=6.8$ Hz, $J_{5',6'}=11.2$ Hz (br d), $J_{6',8'}$=br s.
[q] $J_{(CH_3)_2CH\text{-}7'}=6.9$ Hz, $J_{5',6'}=11.2$ Hz, $J_{6',8'}=2.0$ Hz.

Table 2. The ^{13}C NMR chemical shifts (δ, ppm) for **3**, **5**, **7**, and **9–12** in CF_3COOD at 25 °C

Compound	C-1′	C-2′	C-3′	C-3a′	C-4′	C-5′	C-6′	C-7′	C-8′	C-8a′	Me-1′	Me-4′	$(CH_3)_2$CH-7′	Me_2CH-7′	HC^+- α	C-2,5	C-3,4
3[a]	147.1	138.4	139.4	153.5	156.7	149.8	144.1	172.8	138.3	160.9	12.3	28.0	22.3	40.1	137.0	148.6	140.5
5[a]	146.2	139.2	138.1	152.5	156.3	149.2	143.5	172.1	137.7	160.1	12.0	27.3	21.8	39.1	127.3	157.9	128.5
Difference[b]	+0.9	−0.8	+1.3	+1.0	+0.4	+0.6	+0.6	+0.7	+0.6	+0.8	+0.3	+0.7	+0.5	+1.0	+9.7	−9.3	+12.0
7	146.1	141.7	137.0	155.5	157.3	150.0	145.2	171.6	140.1	161.6	14.1	30.1	24.6	41.9	143.5	141.7,[e] 142.1[f]	144.6,[g] 131.7[h]
Difference[c]	+1.0	−3.3	+2.4	−2.0	−0.6	−0.2	−1.1	+1.2	−1.8	−0.7	−1.8	−2.1	−2.3	−1.8	−6.5		
9	145.6	144.4	136.1	155.1	156.9	149.7	144.9	171.4	139.7	161.7	14.0	29.8	24.6	41.9	133.0	154.9,[e] 154.5[f]	131.5,[g] 117.2[h]
Difference[d]	+0.6	−5.2	+2.0	−2.6	−0.6	−0.5	−1.4	+0.7	−2.0	−1.6	−2.0	−2.5	−2.8	−2.8	−5.7		
10[a]	150.7	138.0	150.6	153.8	159.6	153.2	146.2	177.6	139.6	164.5	13.6	28.9	23.4	41.7	138.4	—	—
11[a]	146.2	140.1	142.1	152.0	156.7	150.2	144.2	174.1	137.9	162.3	11.5	27.6	21.8	39.8	145.2	136.0[i]	133.0,[j] 131.3[k]
12[a]	147.0	141.0	142.1	153.8	157.8	150.6	144.7	173.9	138.6	162.6	12.6	28.6	22.9	40.7	148.0	139.1[l]	133.5[m]

[a] Two 3-guaiazulenylmethylium-ion parts are equivalent.
[b] Difference of the chemical shifts for **3** and **5**.
[c] Difference of the chemical shifts for **3** and **7**.
[d] Difference of the chemical shifts for **5** and **9**.
[e] C-2.
[f] C-5.
[g] C-3.
[h] C-4.
[i] C-1,2.
[j] C-3,6.
[k] C-4,5.
[l] C-1,4.
[m] C-2,3,5,6.

(1.1)>C-8a′ (0.7)>C-4′ (0.6)>C-5′ (0.2) (see Table 2). A comparative study on the UV–vis [λ_{max} (CF_3COOH) nm] spectrum of **3** with that [λ_{max} (CH_3CN) nm] spectrum of **7**[10] showed that, although the longest absorption wavelength of **7** appeared at λ_{max} 497 nm (log ε=4.73), that of **3** was observed at λ_{max} 621 nm (log ε=4.98) with a shoulder band at λ_{max} 593 nm (log ε=4.94) (see Fig. 3). Thus, the elemental analysis and these spectroscopic data for **3** led to the molecular structure, 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (see Chart 2). Along with a facile preparation and the spectroscopic properties of **3**, although the reduction of **7** with $NaBH_4$ in acetonitrile at 25 °C for 40 min gave as high as 92% isolated yield of (3-guaiazulenyl)(2-thienyl)methane[10] (**13**) (see Chart 4), in which a hydride-ion attached to the C-α position of **7**, selectively, the $NaBH_4$-reduction of **3** under the same reaction conditions as for **7** afforded several chromatographically inseparable products, suggesting the formation of different kinds of H^- reduction products, simultaneously. In the previous paper,[8] we reported that the reduction of **10** with zinc powder in trifluoroacetic acid[36] at 0 °C for 5 min under argon gave (*E*)-1,2-di(3-guaiazulenyl)ethylene (**15**) (see Chart 4), efficiently (94% isolated yield). Similarly, the zinc-reduction of **3** in acetone at 25 °C for 20 min under argon afforded compound **16** (red paste; molecular formula: $C_{36}H_{38}S$, determined by the exact FABMS spectrum using 3-nitrobenzyl alcohol as a matrix reagent) in 70% isolated yield.[37] The molecular structure of **16** was presumed to be a mixture of the *E* and *Z* forms of 2,5-bis[di(3-guaiazulenyl)-methylidene]-2,5-dihydrothiophene (see Chart 4); however, it could not be determined, because **16** was unstable under aerobic conditions, gradually converting to a polar resinous substance [brown paste; R_f=0.0 on silica-gel TLC (solv. hexane–AcOEt=8:2, v/v)]. Moreover, from comparative studies on the chemical shifts for the ^{1}H and ^{13}C NMR signals of **3** with those of 2,5-bis[di(3-guaiazulenyl)-methyl]thiophene (**17**) (see Chart 4), which was prepared according to the procedure shown in Section 4.1.3, it was found (i) that all the proton signals of **3** showed larger down-field shifts in comparison with those of **17**; and (ii) that the carbon signals based on the C-1′, 3′, 3a′, 4′–8′, and 8a′ positions of the 3-guaiazulenyl group and the C-3 and 4 positions of the thiophene ring for **3** revealed larger down-field shifts in comparison with those of **17**, suggesting the formation of **3** with a delocalized π-electron system (i.e., with the representative four resonance forms of **C**–**F**) (see Chart 2), whose formation was supported by the $NaBH_4$- and Zn-reduction of **3** along with comparative studies on the UV–vis and NMR (for ^{1}H and ^{13}C) spectral data of **3** with those of **7**.

Compound **5** (84% isolated yield) was dark-purple powder, mp >150 °C [decomp., determined by the thermal analysis (TGA and DTA)], while a solution of **5** in an organic solvent (e.g., CH_3CN, CH_3COCH_3, or CF_3COOH) was blue. A comparative study on the UV–vis [λ_{max} (CF_3COOH) nm] spectrum of **5** with that of **3** showed that, although two specific absorption bands of **3** appeared at λ_{max} 621 and 593sh nm (log ε=4.98 and 4.94), whose spectral pattern was the same as in the cases of 2,5-thiophenediylbis[bis(3-methyl-1-azulenyl)methylium] bis(hexafluorophosphate) [λ_{max} 724 and 602 nm (log ε=4.66 and 4.62)] and 2,5-thiophenediylbis[bis(3,6-di-*tert*-butyl-1-azulenyl)methylium] bis(hexafluorophosphate) [λ_{max} 729 and 594 nm (log ε=4.71 and

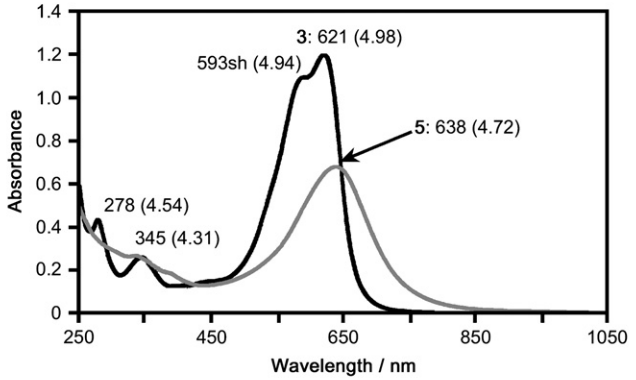
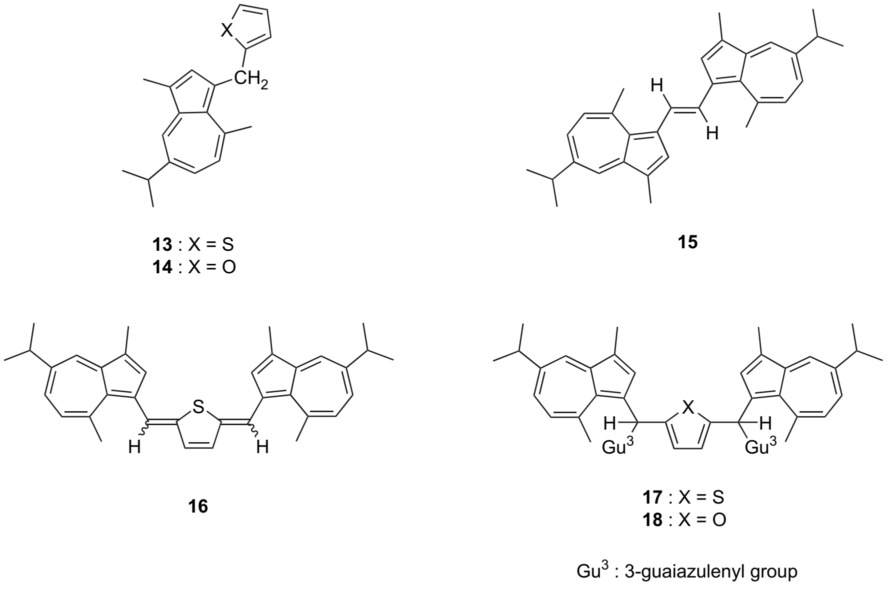


Figure 3. The UV–vis spectra of **3** and **5** in CF_3COOH. Concentrations, **3**: 0.10 g/L (126 μmol/L) and **5**: 0.10 g/L (129 μmol/L). Length of the cell: 0.1 cm each. Log ε values are given in parenthesis.

4.63)],[22] the longest absorption wavelength of **5** was observed at λ_{max} 638 nm (log ε=4.72) (see Fig. 3). It is noteworthy that, although a characteristic UV–vis (CH_3CN) absorption band of **7** appeared at λ_{max} 497 nm (log ε= 4.73), whose spectral pattern and longest absorption wavelength [λ_{max} (CH_3CN) nm (log ε)] resembled those of (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphates (**9**) [the longest absorption wavelength: λ_{max} 499 nm (log ε=4.61)],[10] a characteristic UV–vis spectral pattern and the longest absorption wavelength of **3** did not resemble those of **5**. The IR (KBr) spectrum showed two specific bands based on the counter anion (PF_6^-) at ν_{max} 741 and 482 cm^{-1}, which revealed larger low wavenumber shifts as compared with those of **3** (ν_{max} 837 and 556 cm^{-1}) and **9** (ν_{max} 840 and 559 cm^{-1}).[10] The molecular formula $C_{36}H_{38}O$ for the dicarbenium-ion ($[M-2PF_6]^{2+}$) part was determined by the exact FABMS spectrum using 3-nitrobenzyl alcohol as a matrix reagent. An elemental analysis confirmed the molecular formula $C_{36}H_{38}F_{12}OP_2$. Similarly, as in the cases of **3** and **10**,[8] the 700 MHz ^1H NMR spectrum using CD_3CN as a measurement solvent showed extremely complicated signals,[35] which could not be assigned; however, that spectrum, measured in CF_3COOD, showed proton signals based on two equivalent 3-guaiazulenylmethylium-ion parts, and revealed a proton signal based on the 2,5-furylene part, whose proton signals (δ and J values) were carefully assigned using the first-order analysis and the H–H COSY technique (see Table 1). The 176 MHz ^{13}C NMR (CF_3COOD) spectrum exhibited 17 carbon signals, indicating that the two 3-guaiazulenylmethylium substituents are equivalent, assigned by the HMQC and HMBC techniques (see Table 2). Comparative studies on the chemical shifts (δ, ppm) for the ^1H and ^{13}C NMR signals of the 3-guaiazulenylmethylium-ion part of **5** with those of **9** under the same measurement conditions are shown in Tables 1 and 2. As the results, it was found (i) that the proton signal of the H-2′ (8.65) of **5** coincided with that of **9** (H-2′: 8.68); however, the other proton signals of **5** revealed down-field shifts in comparison with those of **9**; namely, the order of the larger down-field shift was H-5′ ($\Delta\delta$ 0.21 ppm)>H-6′ (0.17)>Me-1′ (0.15)>Me-4′, Me_2CH-7′ (0.12, each)>H-8′ (0.11)>HC^+-α (0.10)>$(CH_3)_2CH$-7′ (0.08) (see Table 1); and (ii) that, although the carbon signals of the C-1′ (146.2), C-3′ (138.1), and C-7′ (172.1) of **5** showed down-field shifts in comparison with those of **9** (C-1′: 145.6, C-3′: 136.1, and C-7′: 171.4), the other carbon signals of **5** revealed up-field shifts in comparison with those of **9**; namely, the order of the larger up-field shift was HC^+-α ($\Delta\delta$ 5.7 ppm)>C-2′ (5.2)>$(CH_3)_2CH$-7′, Me_2CH-7′ (2.8, each)>C-3a′ (2.6)>Me-4′ (2.5)>C-8′, Me-1′ (2.0, each)>C-8a′ (1.6)>C-6′ (1.4)>C-4′ (0.6)>C-5′ (0.5) (see Table 2). Thus, the elemental analysis and these spectroscopic data for **5** led to the molecular structure, 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (see Chart 2). Along with a facile preparation and the spectroscopic properties of **5**, although the reduction of **9** with $NaBH_4$ in acetonitrile at 25 °C for 40 min gave as high as 92% isolated yield of (2-furyl)-(3-guaiazulenyl)methane[10] (**14**) (see Chart 4), in which a hydride-ion attached to the C-α position of **9**, selectively, similarly as in the case of **3**, the $NaBH_4$-reduction of **5** under



13 : X = S
14 : X = O

15

16

17 : X = S
18 : X = O

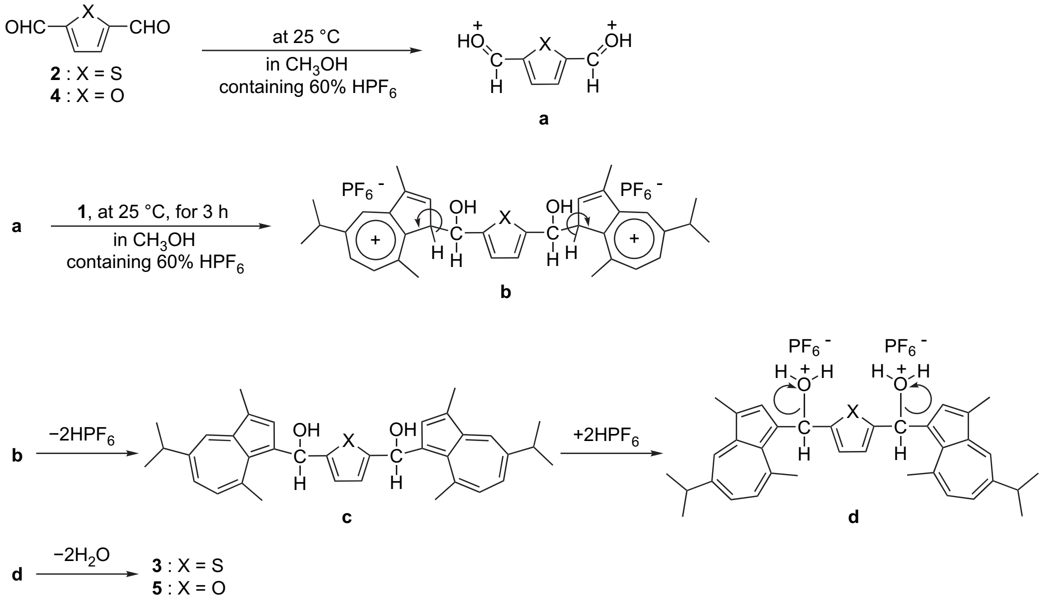
Gu^3 : 3-guaiazulenyl group

Chart 4.

the same reaction conditions as for **3** gave several chromatographically inseparable products, suggesting the formation of different kinds of H$^-$ reduction products, simultaneously. Furthermore, the zinc-reduction of **5** under the same reaction conditions as for **3** afforded a polar resinous substance [reddish-brown paste; R_f=0.0 on silica-gel TLC (solv. hexane–AcOEt=8:2, v/v)]. Moreover, from comparative studies on the chemical shifts for the ^{1}H and ^{13}C NMR signals of **5** with those of 2,5-bis[di(3-guaiazulenyl)methyl]furan (**18**) (see Chart 4), which was prepared according to the procedure shown in Section 4.1.4, it was found (i) that all the proton signals of **5** showed larger down-field shifts in comparison with those of **18**; and (ii) that the carbon signals based on the C-1′, 3′, 3a′, 4′–8′, and 8a′ positions of the 3-guaiazulenyl group and the C-3 and 4 positions of the furan ring for **5** revealed larger down-field shifts in comparison with those of **18**, suggesting the formation of **5** with a delocalized π-electron system (i.e., with the representative four resonance forms of **C**–**F**) (see Chart 2), whose formation was supported by the NaBH$_4$- and Zn-reduction of **5** along with comparative studies on the UV–vis and NMR (for ^{1}H and ^{13}C) spectral data of **5** with those of **9**.

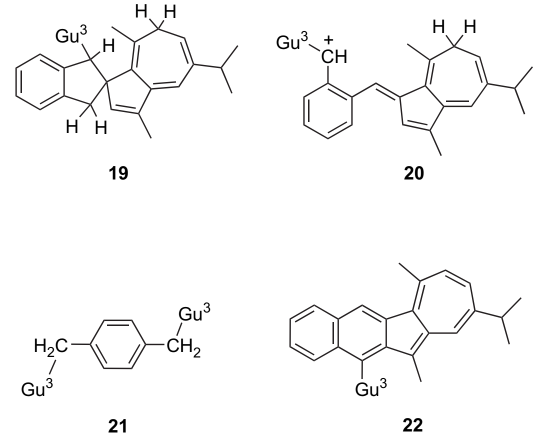
From the molecular structure of the resulting product **3** (or **5**) yielded by the reaction of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) [or furan-2,5-dicarbaldehyde (**4**)] in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h, a plausible reaction pathway for the formation of compound **3** (or **5**) can be inferred as illustrated in Scheme 1; namely, the protonated-compound **a** generated is gradually converted to **3** (or **5**) presumably via the azulenylium-ion form **b**, the secondary-alcohol intermediate **c**, and the dehydration from the oxonium-ion structure **d**.

Comparative studies on the chemical shifts for the ^{1}H and ^{13}C NMR signals of **3** with those of **5** under the same measurement conditions are shown in Tables 1 and 2. As the results, it was found (i) that the proton signal of the H-2′ (8.34) of **3** showed a larger up-field shift in comparison with that of **5** (H-2′: 8.65); however, the proton signals of the HC$^+$-α (8.81) and H-3,4 (7.93) of **3** revealed larger down-field shifts in comparison with those of **5** (HC$^+$-α: 8.44 and H-3,4: 7.67) (see Table 1); and (ii) that, although the carbon signal of the C-2′ (138.4) of **3** showed a slight up-field shift in comparison with that of **5** (C-2′: 139.2), the other carbon signals of the 3-guaiazulenyl group of **3** revealed slight down-field shifts in comparison with those of **5** and, further, the carbon signals of the HC$^+$-α (137.0) and C-3,4 (140.5) of **3** showed larger down-field shifts in comparison with those of **5** (HC$^+$-α: 127.3 and C-3,4: 128.5); however, the carbon signal of the C-2,5 (148.6) of **3** revealed a larger up-field shift in comparison with that of **5** (C-2,5: 157.9) (see Table 2). Moreover, comparative studies on the chemical shifts for the ^{1}H and ^{13}C NMR signals of the 3-guaiazulenylmethylium-ion parts for **3** and **5** with those of the following delocalized dicarbenium-ion compounds, i.e., α,α′-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate)[8] (**10**), 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate)[4] (**11**), and 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate)[32] (**12**), under the same measurement conditions as for **3** and **5** are shown in Tables 1 and 2. Interestingly, similarly as in the cases of **3** and **5**, the 500 MHz ^{1}H NMR spectrum of **10** using CD$_3$CN as a measurement solvent showed extremely complicated signals,[35] which could not be assigned; however, those spectra of **11**[4] and **12**,[32] measured in CD$_3$CN, showed proton signals based on two equivalent 3-guaiazulenylmethylium substituents, respectively, and revealed proton signals based on the 1,2-phenylene part of **11** and the 1,4-phenylene part of **12**. Along with the above results, similarly as in the cases of **3** and **5**, the NaBH$_4$-reduction of **10** under the same reaction conditions as for **3** and **5** gave several chromatographically inseparable products, suggesting the formation of different kinds of H$^-$ reduction products, simultaneously; however, the NaBH$_4$-reductions of **11** and **12** afforded spiro[1-(3-guaiazulenyl)-indane-2,1′-1′*H*,7′*H*-3′,8′-dimethyl-5′-isopropylazulene][4] (**19**)



Scheme 1. A plausible reaction pathway for the formation of **3** (or **5**) yielded by the reaction of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) [or furan-2,5-dicarbaldehyde (**4**)] in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h.

(92% isolated yield) presumably via the intermediate **20**[4] from **11** and 1,4-bis(3-guaiazulenylmethyl)benzene[9] (**21**) (80% isolated yield), in which two hydride-ions attached to the HC$^+$-α and α' positions of **12**, selectively (see Chart 5). Moreover, although the zinc-reduction of **11** in acetonitrile at 0 °C for 10 min under aerobic conditions gave 6,11-dimethyl-12-(3-guaiazulenyl)-9-isopropylnaphtho[2,3-*a*]azulene[2] (**22**) (see Chart 5) in 11% isolated yield, the zinc-reduction of **12** under the same reaction conditions as for **11** afforded several chromatographically inseparable products, simultaneously. Thus, an apparent difference between the NaBH$_4$- and Zn-reduction behavior of **10–12** was observed.



Gu^3 : 3-guaiazulenyl group

Chart 5.

2.2. The optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for 3 and 5

In the previous paper,[4] we reported the crystal structure of 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**11**) (see Fig. 4). From the result of an X-ray crystallographic analysis of **11**, it was found (i) that two adjacent 3-guaiazulenylmethylium substituents twisted to the same side from the benzene ring; (ii) that, although a 3-guaiazulenylmethylium substituted at the C-1 position of the benzene ring was planar, another 3-guaiazulenylmethylium substituted at the C-2 position of the benzene ring was not planar; and (iii) that the benzene ring was slightly distorted, owing to the influence of large steric hindrance and repulsion between two adjacent 3-guaiazulenylmethylium substituents and the benzene ring and, further, owing to the influence of electrostatic repulsion between two adjacent carbenium-ions. Along with the clarification of the crystal structure of **11**, the crystal structure of 1,4-phenylenebis-(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**12**), which was prepared according to the procedure shown in Ref. 32, was measured by means of the X-ray diffraction. As the result, although an X-ray crystallographic analysis of **12**, producing accurate structural parameters, has not yet been achieved, because it was very difficult to obtain a single crystal suitable for this purpose, the molecular structure of **12** established on the basis of elemental analysis and NMR spectral data[32] could be determined as shown in Figure 4 (see Ref. 33). Similarly, as in the case of **11**, two 3-guaiazulenylmethylium substituted at the C-1 and 4 positions of the benzene ring of **12** twisted to the same side from the benzene

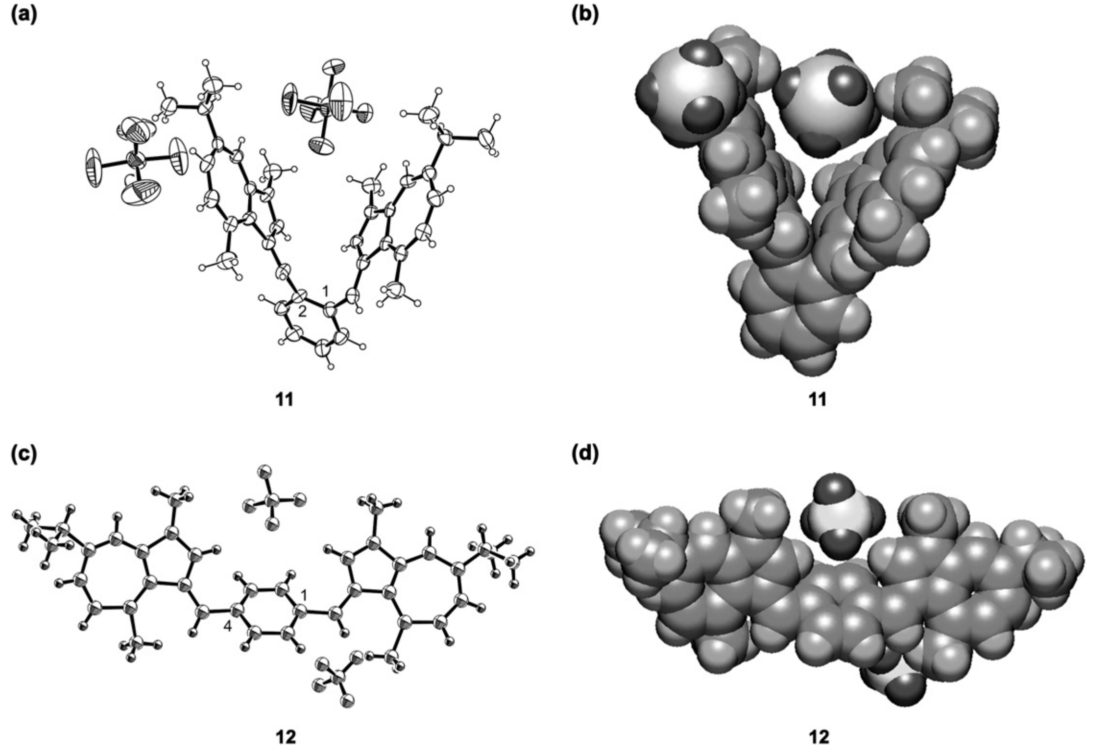


Figure 4. (a) The ORTEP drawing of **11** (30% probability thermal ellipsoids).[4] (b) The crystal structure of **11** shown using a space-filling mode. (c) The crystal structure of **12**[33] shown using a ball-and-stick mode. (d) The crystal structure of **12**[33] shown using a space-filling mode.

ring. Along with the crystal structures of **11** and **12**, from a comparative study on the bond lengths of the crystal structures of (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate[10] (**7**) and (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate[10] (**9**) with those of the optimized (3-guaiazulenyl)(2-thienyl)methylium- and (2-furyl)(3-guaiazulenyl)methylium-ion structures calculated by a WinMOPAC (version 3.0) program using PM3, AM1, and MNDOD as semiempirical Hamiltonians, the bond lengths calculated using PM3 more resembled those of the crystal structures of **7** and **9**, respectively, in comparison with those calculated using AM1 and MNDOD (see Table 3). Thus, referring to the results of the X-ray crystallographic analyses of **7**, **9**, **11**,[4] and **12**,[33] the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5**, whose two 3-guaiazulenylmethylium-ion parts twisted to the same side from the thiophene and furan rings, respectively, have been calculated using PM3 (see Fig. 5),[34] because it was very difficult to obtain single crystals of **3** and **5** suitable for the X-ray crystallographic analysis. As the results, similarly as in the cases of the crystal structures of **7** and **9** (see Fig. 1), it could be inferred that the steric hindrance and repulsion between the sulfur atom of the thiophene ring and the H-2′ hydrogen atoms of two 3-guaiazulenylmethylium substituents for **3** were much larger than those between the oxygen atom of the furan ring and the H-2′ hydrogen atoms of two 3-guaiazulenylmethylium substituents for **5**, whose results were indirectly supported by the difference of the chemical shifts for the ^{1}H and ^{13}C NMR signals of **3** (H-2′: 8.34; C-2′: 138.4) and **5** (H-2′: 8.65; C-2′: 139.2) (see Tables 1 and 2).

2.3. Electrochemical behavior of 3 and 5

We have been interested further in the electrochemical properties of the dicarbenium-ions **3** and **5** with a view to a comparative study on those of them. The electrochemical behavior of **3** and **5** was, therefore, measured by means of the CV and DPV [potential (V) vs SCE] in CH$_3$CN containing 0.1 M [n-Bu$_4$N]PF$_6$ as a supporting electrolyte. From a comparative study on the reduction potentials of **3** and **5** with those of the previously-documented monocarbenium-ions **7**[10] and **9**[10] under the same measurement conditions, it could be inferred that, although the CV and DPV waves of **3** and **5** did not appear clearly as compared with those of **7** and **9**, compounds **3** and **5** underwent two-electron reduction, respectively, at the potentials of −0.31 V (E_{pc}, irreversible) by CV (−0.25 V by DPV) for **3** and −0.18 V (E_{pc}, irreversible) by CV (−0.07 V by DPV) for **5** as shown in Figure 6, yielding the quinoid compounds, 2,5-bis[di(3-guaiazulenyl)-methylidene]-2,5-dihydrothiophene (**16**) (see Section 2.2 and Chart 4) and 2,5-bis[di(3-guaiazulenyl)methylidene]-2,5-dihydrofuran, via the corresponding biradical-species. Thus, although **3** is less susceptible to reduction as compared with **7** [−0.22 V (E_{pc}, irreversible) by CV (−0.16 V by DPV)], **5** is susceptible to reduction as compared with **9** [−0.27 V (E_{pc}, irreversible) by CV (−0.21 V by DPV)], owing to the difference in electron affinity (corresponding to LUMO) based on those molecular structures.

3. Conclusion

We have reported the following five points in this paper: (i) the reaction of guaiazulene (**1**) with thiophene-2,5-dicarbaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 3 h gave as high as 90% isolated yield of the delocalized dicarbenium-ion compound, 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**3**); (ii) similarly, the reaction of **1** with furan-2,5-dicarbaldehyde (**4**) under the same conditions as the above reaction afforded the corresponding dicarbenium-ion compound, 2,5-furylenebis(3-guaiazulenylmethylium)

Table 3. The selected bond lengths (Å) of the X-ray crystal structures of (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate[10] (**7**) and (2-furyl)-(3-guaiazulenyl)methylium hexafluorophosphate[10] (**9**) and the optimized (3-guaiazulenyl)(2-thienyl)methylium- and (2-furyl)(3-guaiazulenyl)methylium-ion structures

Atom	**7** (X-ray)	**7** (PM3)	**7** (AM1)	**7** (MNDOD)	**9** (X-ray)	**9** (PM3)	**9** (AM1)	**9** (MNDOD)
C1′–C2′	1.352	1.364	1.372	1.379	1.321	1.365	1.372	1.379
C2′–C3′	1.447	1.458	1.462	1.468	1.456	1.458	1.465	1.470
C3′–C3a′	1.475	1.474	1.473	1.484	1.475	1.475	1.477	1.489
C3a′–C4′	1.409	1.390	1.392	1.416	1.403	1.390	1.389	1.412
C4′–C5′	1.406	1.406	1.404	1.416	1.399	1.407	1.407	1.420
C5′–C6′	1.372	1.374	1.380	1.399	1.366	1.374	1.377	1.396
C6′–C7′	1.402	1.403	1.399	1.414	1.402	1.403	1.401	1.417
C7′–C8′	1.392	1.388	1.391	1.412	1.374	1.387	1.390	1.410
C8′–C8a′	1.390	1.389	1.385	1.406	1.395	1.389	1.387	1.407
C8a′–C1′	1.452	1.460	1.467	1.477	1.459	1.458	1.467	1.476
C3a′–C8a′	1.445	1.441	1.448	1.462	1.445	1.442	1.448	1.462
C3′–Cα	1.363	1.361	1.364	1.383	1.373	1.361	1.359	1.377
Cα–C2	1.433	1.429	1.416	1.438	1.412	1.423	1.417	1.439
C2–C3	1.413	1.392	1.408	1.423	1.363	1.395	1.400	1.416
C3–C4	1.404	1.421	1.413	1.426	1.397	1.425	1.433	1.428
C4–C5	1.342	1.373	1.390	1.402	1.338	1.382	1.389	1.401
C5–X1	1.707	1.708	1.645	1.708	1.363	1.363	1.384	1.355
X1–C2	1.721	1.743	1.687	1.738	1.378	1.396	1.410	1.378

Compound **7**: X1=S. Compound **9**: X1=O. The following MO calculation program and calculation conditions were used (i.e., the software: WinMOPAC version 3.0 developed by Fujitsu Ltd., Japan; semiempirical Hamiltonian: PM3, AM1, or MNDOD; and keywords: CHARGE=1, PRECISE, VECTORS, ALLVEC, BONDS, GEO-OK, EF, PL, LET, T=10D, GNORM=10^{-4}, and SCFCRT=10^{-10}). The final values of the gradient norms of the optimized (3-guaiazulenyl)(2-thienyl)methylium- and (2-furyl)(3-guaiazulenyl)methylium-ion structures; PM3: 0.017 and 0.008; AM1: 0.018 and 0.010; MNDOD: 0.012 and 0.013, respectively.

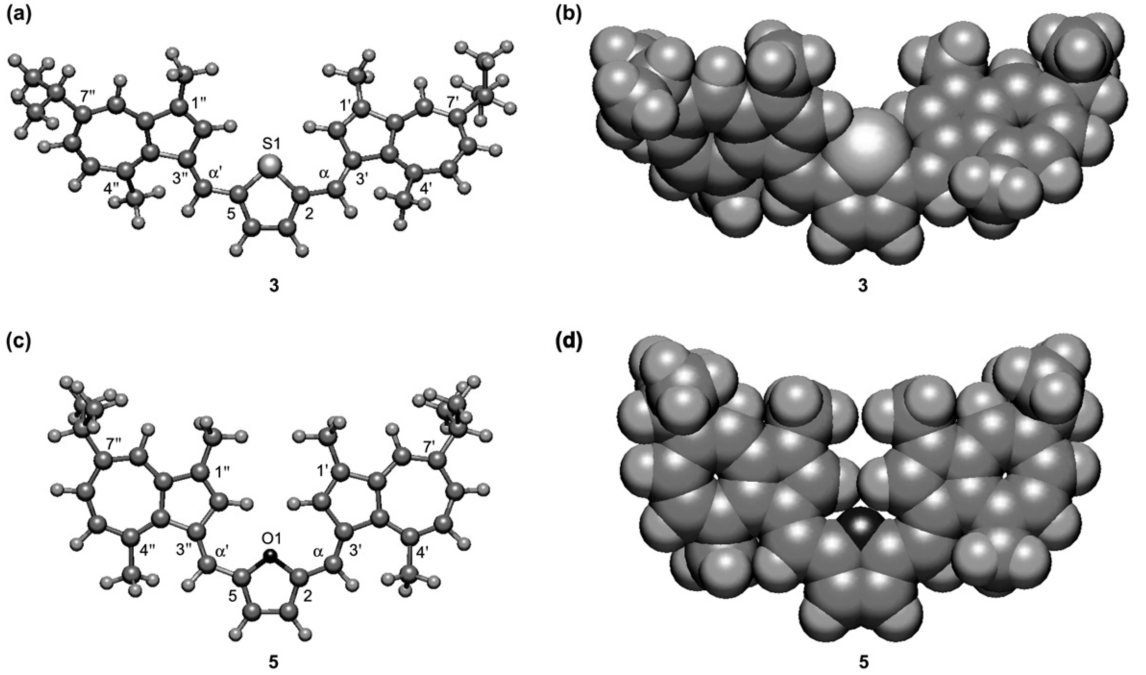


Figure 5. (a) The optimized 2,5-thienylenebis(3-guaiazulenylmethylium)-ion structure for **3**[34] shown using a ball-and-stick mode. The selected bond lengths (Å): S1–C2, 1.738; C2–C3, 1.384; C3–C4, 1.422; C4–C5, 1.383; C5–S1, 1.738; C2–Cα, 1.444; C5–Cα′, 1.444; C1′–C2′, 1.359; C2′–C3′, 1.465; C3′–C3a′, 1.484; C3a′–C4′, 1.391; C4′–C5′, 1.408; C5′–C6′, 1.376; C6′–C7′, 1.401; C7′–C8′, 1.389; C8′–C8a′, 1.387; C8a′–C1′, 1.469; C8a′–C3a′, 1.435; C3′–Cα, 1.351; C1″–C2″, 1.359; C2″–C3″, 1.465; C3″–C3a″, 1.484; C3a″–C4″, 1.391; C4″–C5″, 1.409; C5″–C6″, 1.375; C6″–C7″, 1.401; C7″–C8″, 1.389; C8″–C8a″, 1.388; C8a″–C1″, 1.469; C8a″–C3a″, 1.435; C3″–Cα′, 1.351. (b) The optimized 2,5-thienylenebis(3-guaiazulenylmethylium)-ion structure for **3**[34] shown using a space-filling mode. (c) The optimized 2,5-furylenebis(3-guaiazulenylmethylium)-ion structure for **5**[34] shown using a ball-and-stick mode. The selected bond lengths (Å): O1–C2, 1.385; C2–C3, 1.391; C3–C4, 1.427; C4–C5, 1.390; C5–O1, 1.385; C2–Cα, 1.439; C5–Cα′, 1.439; C1′–C2′, 1.357; C2′–C3′, 1.463; C3′–C3a′, 1.485; C3a′–C4′, 1.390; C4′–C5′, 1.409; C5′–C6′, 1.374; C6′–C7′, 1.404; C7′–C8′, 1.391; C8′–C8a′, 1.387; C8a′–C1′, 1.470; C8a′–C3a′, 1.437; C3′–Cα, 1.354; C1″–C2″, 1.358; C2″–C3″, 1.463; C3″–C3a″, 1.484; C3a″–C4″, 1.389; C4″–C5″, 1.409; C5″–C6″, 1.374; C6″–C7″, 1.404; C7″–C8″, 1.391; C8″–C8a″, 1.386; C8a″–C1″, 1.470; C8a″–C3a″, 1.436; C3″–Cα′, 1.353. (d) The optimized 2,5-furylenebis(3-guaiazulenylmethylium)-ion structure for **5**[34] shown using a space-filling mode.

bis(hexafluorophosphate) (**5**), in 84% isolated yield; (iii) along with a facile preparation and the spectroscopic properties of **3** and **5**, comparative studies on the ^{1}H and ^{13}C NMR spectral and chemical properties of **3** and **5** with those of the delocalized mono- and dicarbenium-ion compounds [i.e., (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate (**7**), (2-furyl)(3-guaiazulenyl)methylium hexafluorophosphate (**9**), α,α′-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**10**), 1,2-phenylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (**11**), and 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate) (**12**)] were reported, suggesting the formation of **3** and **5** with the representative four resonance forms of **C**–**F** (see Chart 2); (iv) referring to the results of the X-ray crystallographic analyses of **7**, **9**, **11**, and **12**, the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5**, calculated by a WinMOPAC (version 3.0) program using PM3 as a semiempirical Hamiltonian, were described; and (v) the CV and DPV data suggested that **3** and **5** underwent two-electron reduction, yielding the quinoid compounds, 2,5-bis[di(3-guaiazulenyl)methylidene]-2,5-dihydrothiophene and 2,5-bis[di(3-guaiazulenyl)methylidene]-2,5-dihydrofuran, respectively, via the corresponding biradical-species and, further, those indicated that, although **3** was less susceptible to reduction as compared with **7**, **5** was susceptible to reduction as compared with **9**.

4. Experimental

4.1. General

Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder, respectively. FABMS 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, respectively. NMR spectra were recorded with a JEOL GX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C), JNM-ECA600 (600 MHz for ^{1}H and 150 MHz for ^{13}C), or JNM-ECA700 (700 MHz for ^{1}H and 176 MHz for ^{13}C) cryospectrometer at 25 °C. Cyclic and differential pulse voltammograms were measured by an ALS Model 600 electrochemical analyzer.

4.1.1. Preparation of 2,5-thienylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (3). To a solution of commercially available guaiazulene (**1**) (238 mg, 1.20 mmol) in methanol (4.0 mL) was added a solution of commercially available thiophene-2,5-dicarbaldehyde (**2**) (53 mg, 0.38 mmol) in methanol (1.5 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.1 mL). The mixture was stirred at 25 °C for 3 h, precipitating a dark-brown solid of **3**, and then was centrifuged at 2.5 krpm for

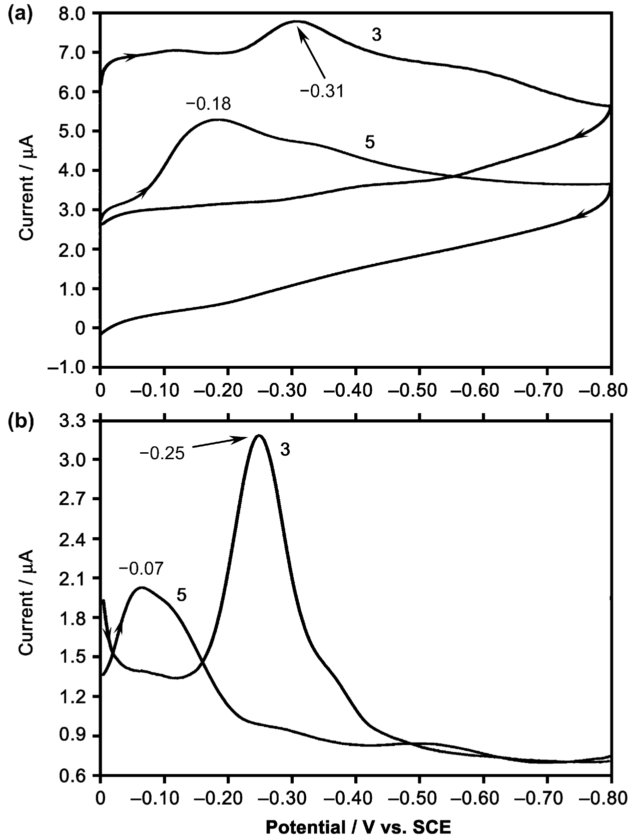


Figure 6. (a) Cyclic and (b) differential pulse voltammograms of **3** (3.0 mg, 3.8 μmol) and **5** (3.0 mg, 3.9 μmol) in 0.1 M [*n*-Bu$_4$N]PF$_6$, CH$_3$CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes, respectively; scan rates 100 mV/s at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (E_p) by DPV and +0.40 V ($E_{1/2}$) by CV under the same electrochemical conditions as for **3** and **5**.

1 min. The thus-obtained crude product **3** was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **3** as stable crystals (271 mg, 0.34 mmol, 90% yield).

Compound **3**: dark-green needles, mp >130 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 54.66; H, 4.64%. Calcd for $C_{36}H_{38}F_{12}P_2S$: C, 54.55; H, 4.83%. UV–vis λ_{max} (CF_3COOH) nm (log ε): 278 (4.54), 345 (4.31), 593sh (4.94), and 621 (4.98). IR ν_{max} (KBr) cm^{-1}: 837 and 556 (PF_6^-). Exact FABMS (3-nitrobenzyl alcohol matrix), found: *m*/*z* 502.2719; calcd for $C_{36}H_{38}S$: $[M-2PF_6]^{2+}$, *m*/*z* 502.2695. 700 MHz ^{1}H NMR (CF_3COOD): see Table 1. 176 MHz ^{13}C NMR (CF_3COOD): see Table 2.

4.1.2. Preparation of 2,5-furylenebis(3-guaiazulenylmethylium) bis(hexafluorophosphate) (5). To a solution of guaiazulene (**1**) (100 mg, 0.50 mmol) in methanol (2.0 mL) was added a solution of commercially available furan-2,5-dicarbaldehyde (**4**) (24 mg, 0.19 mmol) in methanol (1.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.1 mL). The mixture was stirred at 25 °C for 3 h, precipitating a dark-purple solid of **5**, and then was centrifuged at 2.5 krpm for 1 min. The thus-obtained crude product **5** was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **5** as a stable powder (126 mg, 0.16 mmol, 84% yield).

Compound **5**: dark-purple powder, mp >150 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 55.71; H, 4.96%. Calcd for $C_{36}H_{38}F_{12}OP_2$: C, 55.68; H, 4.93%. UV–vis λ_{max} (CF_3COOH) nm (log ε): 638 (4.72). IR ν_{max} (KBr) cm^{-1}: 741 and 482 (PF_6^-). Exact FABMS (3-nitrobenzyl alcohol matrix), found: *m*/*z* 486.2924; calcd for $C_{36}H_{38}O$: $[M-2PF_6]^{2+}$, *m*/*z* 486.2922. 700 MHz ^{1}H NMR (CF_3COOD): see Table 1. 176 MHz ^{13}C NMR (CF_3COOD): see Table 2.

4.1.3. Preparation of 2,5-bis[di(3-guaiazulenyl)methyl]-thiophene (17). To a solution of guaiazulene (**1**) (176 mg, 0.89 mmol) in acetic acid (1.5 mL) was added a solution of thiophene-2,5-dicarbaldehyde (**2**) (30 mg, 0.21 mmol) in a mixed solvent (1.5 mL) of acetic acid and trifluoroacetic acid (1:2, v/v). The mixture was stirred at 25 °C for 2 h under argon. After the reaction, the reactant was carefully neutralized with aqueous $NaHCO_3$, and extracted with dichloromethane (3×10 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was purified by alumina column chromatography with benzene–hexane (95:5, v/v) as an eluant. The obtained crude product **17** was recrystallized from dichloromethane–methanol (1:5, v/v) (several times) to provide pure **17** as stable crystals (162 mg, 0.18 mmol, 84% yield).

Compound **17**: dark-blue plates [R_f=0.71 on silica-gel TLC (solv. benzene–hexane=95:5, v/v)], mp>200 °C [decomp., determined by thermal analysis (TGA and DTA)]. Exact FABMS (3-nitrobenzyl alcohol matrix), found: *m*/*z* 896.5368; calcd for $C_{66}H_{72}S$: M$^+$, *m*/*z* 896.5355. 500 MHz ^{1}H NMR (CD_2Cl_2), signals based on two equivalent di(3-guaiazulenyl)methyl groups: δ 1.33 (24H, d, *J*=6.9 Hz, (CH_3)$_2$CH-7′), 2.53 (12H, s, Me-1′), 2.90 (12H, s, Me-4′), 3.00 (4H, sept, *J*=6.9 Hz, Me$_2$C*H*-7′), 6.80 (4H, d, *J*=10.9 Hz, H-5′), 7.17 (4H, s, H-2′), 7.24 (4H, dd, *J*=10.9, 2.0 Hz, H-6′), 7.31 (2H, s, $>$CH-2,5), and 8.08 (4H, d, *J*=2.0 Hz, H-8′); a signal based on the thiophene ring: δ 6.14 (2H, s, H-3,4). 125 MHz ^{13}C NMR (CD_2Cl_2): δ 151.9 (C-2,5), 144.7 (C-4′), 140.2 (C-2′), 138.9 (C-7′), 137.4 (C-8a′), 134.4 (C-6′), 133.4 (C-8′), 131.4 (C-3a′), 131.2 (C-3′), 126.3 (C-5′), 124.9 (C-3,4), 123.6 (C-1′), 42.5 ($>$CH-2,5), 37.3 (Me$_2$*C*H-7′), 26.3 (Me-4′), 24.0 ((*C*H$_3$)$_2$CH-7′), and 12.5 (Me-1′), indicating two di(3-guaiazulenyl)methyl groups are equivalent.

4.1.4. Preparation of 2,5-bis[di(3-guaiazulenyl)methyl]-furan (18). To a solution of guaiazulene (**1**) (201 mg, 1.02 mmol) in acetic acid (1.5 mL) was added a solution of furan-2,5-dicarbaldehyde (**4**) (30 mg, 0.24 mmol) in a mixed solvent (1.5 mL) of acetic acid and trifluoroacetic acid (1:2, v/v). The mixture was stirred at 25 °C for 2 h under argon. After the reaction, the reactant was carefully neutralized with aqueous $NaHCO_3$, and extracted with dichloromethane (3×10 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was purified by alumina column chromatography with benzene–hexane (95:5, v/v) as an eluant. The obtained crude product **18** was recrystallized from dichloromethane–methanol (1:5, v/v) (several times) to provide pure **18** as stable crystals (89 mg, 0.10 mmol, 42% yield).

Compound **18**: dark-blue prisms [R_f=0.73 on silica-gel TLC (solv. benzene–hexane=95:5, v/v)], mp >200 °C [decomp., determined by thermal analysis (TGA and DTA)]. Exact FABMS (3-nitrobenzyl alcohol matrix), found: *m/z* 880.5590; calcd for $C_{66}H_{72}O$: M^+, *m/z* 880.5584. 600 MHz ^1H NMR (CD_2Cl_2), signals based on two equivalent di(3-guaiazulenyl)methyl groups: δ 1.33 (24H, d, J=6.9 Hz, $(CH_3)_2CH$-7′), 2.54 (12H, s, Me-1′), 2.86 (12H, s, Me-4′), 3.01 (4H, sept, J=6.9 Hz, Me_2CH-7′), 6.80 (4H, d, J=10.9 Hz, H-5′), 7.08 (2H, s, >CH-2,5), 7.09 (4H, br s, H-2′), 7.25 (4H, dd, J=10.9, 2.2 Hz, H-6′), and 8.09 (4H, d, J=2.2 Hz, H-8′); a signal based on the furan ring: δ 5.28 (2H, s, H-3,4). 150 MHz ^{13}C NMR (CD_2Cl_2): δ 158.8 (C-2,5), 144.7 (C-4′), 139.8 (C-2′), 138.7 (C-7′), 137.4 (C-8a′), 134.4 (C-6′), 133.3 (C-8′), 131.6 (C-3a′), 129.2 (C-3′), 126.3 (C-5′), 123.6 (C-1′), 109.3 (C-3,4), 41.8 (>CH-2,5), 37.3 (Me_2CH-7′), 26.1 (Me-4′), 24.0 ($(CH_3)_2CH$-7′), and 12.5 (Me-1′), indicating two di(3-guaiazulenyl)methyl groups are equivalent.

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32. Compound **12** was prepared by the following procedure: to a solution of guaiazulene (**1**) (30 mg, 0.15 mmol) in acetic acid (0.5 mL) was added a solution of terephthalaldehyde (10 mg, 0.07 mmol) in acetic acid (0.5 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.24 mL). The mixture was stirred at 25 °C for 2 h. After the reaction, diethyl ether (5.0 mL) was slowly added and the mixture was allowed to stand at 25 °C, precipitating a dark-red solid of **12**, and then was centrifuged at 2 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide

pure **12** as very thin single crystals (24 mg, 0.36 mmol, 51% yield). Compound **12**: dark-red plates, mp >218 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 67.52; H, 6.02%. Calcd for $C_{38}H_{40}B_2F_8$: C, 68.08; H, 6.01%. 500 MHz ^{1}H NMR (CD_3CN): δ 1.49 (12H, d, J=7.0 Hz, $(CH_3)_2$CH-7′,7″), 2.56 (6H, br s, Me-1′,1″), 3.42 (6H, s, Me-4′,4″), 3.54 (2H, sept, J=7.0 Hz, Me_2CH-7′,7″), 8.02 (6H, s, H-2,3,5,6,2′,2″), 8.49 (2H, dd, J=11.0, 2.0 Hz, H-6′,6″), 8.61 (2H, d, J=11.0 Hz, H-5′,5″), 8.63 (2H, d, J=2.0 Hz, H-8′,8″), and 8.81 (2H, br s, HC^+-α,α'). 125 MHz ^{13}C NMR (CD_3CN, determined by HMQC and HMBC techniques): δ 173.2 (C-7′,7″), 162.2 (C-8a′,8a″), 158.6 (C-4′,4″), 153.9 (C-3a′,3a″), 151.6 (C-5′,5″), 148.2 (HC^+-α,α'), 147.5 (C-1′,1″), 145.6 (C-6′,6″), 142.2 (C-3′,3″), 140.9 (C-2′,2″), 140.2 (C-8′,8″), 139.4 (C-1,4), 134.1 (C-2,3,5,6), 40.5 (Me_2CH-7′,7″), 29.8 (Me-4′,4″), 23.8 ($(CH_3)_2$CH-7′,7″), and 14.0 (Me-1′,1″).

33. Although the ORTEP drawing of **12** based on the X-ray crystallographic analysis showed a slight bond disorder, the crystal structure of **12**, indicating the molecular structure of 1,4-phenylenebis(3-guaiazulenylmethylium) bis(tetrafluoroborate), is shown in Figure 4. A total of 6101 reflections with $2\theta_{max}$=50.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å, rotating anode: 50 kV, 180 mA) at 296 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 621593. Crystallographic data for **12**: $C_{38}H_{40}B_2F_8$ (FW=670.34), dark-red prism (the crystal size, 0.20×0.20×0.20 mm^3), triclinic, $P\bar{1}$(#2), a=10.869(2) Å, b=18.228(3) Å, c=9.632(2) Å, α=93.01(2)°, β=95.04(1)°, γ=99.98(1)°, V=1867.6(6) Å^3, Z=3, D_{calcd}=1.788 g/cm^3, μ(Mo Kα)=1.42 cm^{-1}, scan width=(1.21+0.30 tan θ)°, scan mode=$\omega-2\theta$, scan rate=4.0°/min, measured reflections=6101, observed reflections=5724, no. of parameters=433, $R1$=0.244, $wR2$=0.560, and goodness of fit indicator=3.92. An X-ray crystallographic analysis of **12**, producing accurate structural parameters, is further currently under intensive investigation.
34. The following MO calculation program and calculation conditions were used for **3** and **5** (i.e., the software: WinMOPAC version 3.0 developed by Fujitsu Ltd., Japan; semiempirical Hamiltonian: PM3; and keywords: CHARGE=2, PRECISE, VECTORS, ALLVEC, BONDS, GEO-OK, EF, PL, LET, T=10D, GNORM=10^{-4}, and SCFCRT=10^{-10}). The final values of the gradient norms of the optimized 2,5-thienylenebis(3-guaiazulenylmethylium)- and 2,5-furylenebis(3-guaiazulenylmethylium)-ion structures for **3** and **5** showed 0.031 and 0.017, respectively.
35. After the ^{1}H NMR measurement in CD_3CN, the pure sample without decomposition was recovered, quantitatively, by the recrystallization.
36. The reduction of **10** with zinc powder in acetone under the same reaction conditions as for **3** also afforded **15**, quantitatively.
37. Compound **16** was prepared by the following procedure: to a solution of **3** (54 mg, 0.07 mmol) in acetone (5.0 mL) was added a zinc powder (350 mg, 5.4 mmol) under argon. The mixture was stirred at 25 °C for 20 min. After the reaction, the zinc powder was removed by using a centrifugal separator. The reaction solution was evaporated in vacuo, giving a red paste. The residue thus obtained was carefully separated by alumina column chromatography with hexane–ethyl acetate (8:2, v/v) as an eluant (several times) to provide pure **16** (24 mg, 0.48 mmol, 70% yield). Compound **16**: red paste [R_f=0.47 on silica-gel TLC (solv. hexane–AcOEt=8:2, v/v)]. Exact FABMS (3-nitrobenzyl alcohol matrix), found: m/z 502.2715; calcd for $C_{36}H_{38}S$: M$^+$, m/z 502.2695. UV–vis λ_{max} (CH_2Cl_2) nm (log ε): 246 (4.53), 292 (4.57), and 512 (3.95).