

Preparation and Characteristic Properties of 1,4-Bis(3-guaiazulenylmethylium)benzene Bis(hexafluorophosphate)

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Reaction of guaiazulene (**1**) with a 0.5 molar amount of terephthalaldehyde in acetic acid in the presence of hydrochloric acid at 25 °C for 10 min under aerobic conditions selectively affords 1,4-bis(3-guaiazulenylmethylium)benzene dichloride (**2**), which upon treatment with hexafluorophosphoric acid quantitatively forms the title bis(hexafluorophosphate) **3** as stable crystals.

As a series of basic studies on the creation of novel functional materials with delocalized π -electron systems and on their potential utility, we have been particularly interested in the molecular structures of quinodimethanes possessing azulenyl groups (as a representative example of nonbenzenoid aromatics, which plays as an electron donor) at C-7 and C-8 positions, and have been undertaking a highly efficient preparation of those azulenylquinodimethanes, recently.¹ During the course of the investigations, we have discovered that the reaction of guaiazulene (**1**) with terephthalaldehyde in acetic acid in the presence of hydrochloric acid at 25 °C for 10 min under aerobic conditions selectively afforded the dicarbenium compound, 1,4-bis(3-guaiazulenylmethylium)benzene dichloride (**2**), which upon treatment with hexafluorophosphoric acid quantitatively forms the title bis(hexafluorophosphate) **3** as stable crystals.² It is expected that compound **3** is converted into 7,8-di(3-guaiazulenyl)-*p*-quinodimethane.³ On the other hand, Reid et al. have already reported that the reaction of guaiazulene with aromatic aldehydes in dry ether containing hydrogen chloride gave 3-benzylideneguaiazulene salts,⁴ and which were further converted into the corresponding diazulenylmethanes, respectively.⁵ In addition, Asao and his co-workers reported synthesis and characteristic properties (e.g., pK_R^+ values) of several mono-, di- and tricarbeniums stabilized by azulene rings in detail.⁶ We wish to describe herein a facile preparation and characteristic properties of novel dicarbenium compounds **2** and **3** obtained from naturally occurring guaiazulene, which enabled us to compare with the characteristic properties of the dicarbenium compounds, 1,3- and 1,4-bis(diazulenylmethyl-

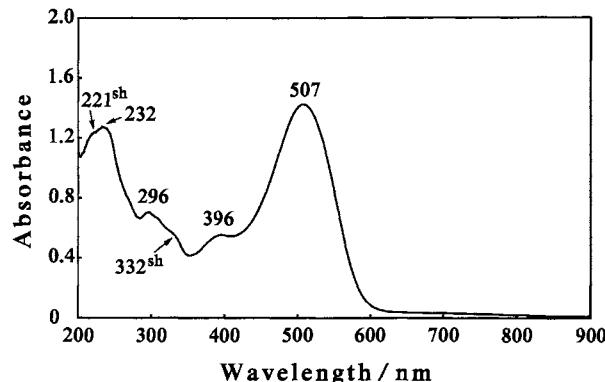
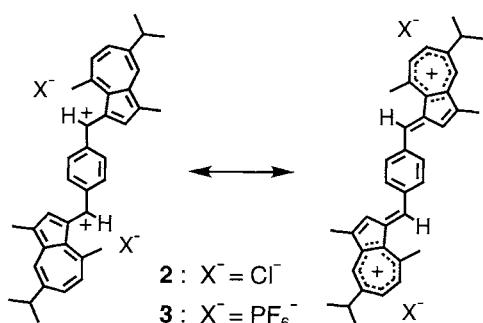


Figure 1. The UV-visible spectrum of compound **3** in CH₃CN. Concentration, 0.022 g/L; length of the cell, 1 cm.

ium)benzene bis(hexafluorophosphates).^{6a}

1,4-Bis(3-guaiazulenylmethylium)benzene bis(hexafluorophosphate) (**3**) was prepared by the following procedures: To a solution of guaiazulene (**1**) (12 mg, 61 μ mol) dissolved in acetic acid (0.5 mL) was added a solution of terephthalaldehyde (4 mg, 30 μ mol) dissolved in acetic acid (0.5 mL) containing hydrochloric acid (35% aqueous solution, 45 μ L). The mixture was stirred at 25 °C for 10 min under aerobic conditions, giving 1,4-bis(3-guaiazulenylmethylium)benzene dichloride (**2**)⁷ as a sole product. Addition of hexafluorophosphoric acid (60% aqueous solution, 100 μ L) to the reactant solution led to the precipitation of a reddish-brown solid, which was centrifuged at 2 krpm for 1 min. The crude product thus obtained was carefully washed with cold water, dried well in a vacuum desiccator, and further recrystallized from acetone-hexane (2:3, v/v) (several times) to provide pure compound **3** as stable crystals (17 mg, 72% yield), whose structure was established on the basis of the elemental analysis and the spectroscopic data [UV-visible, FAB-MS, ¹H- and ¹³C-NMR including their 2D NMR (H-H COSY and C-H COSY)].

Compound **3** was reddish-brown prisms, mp > 150 °C [decomp, determined by the thermal analysis (TGA and DTA)]. The UV-visible spectrum is shown in Figure 1: λ_{max} (CH₃CN) nm (log ϵ), 221sh (4.65), 232(4.66), 296(4.40), 332sh(4.29), 396(4.30), and 507(4.71). No characteristic absorption bands for guaiazulene were observed, indicating the formation of a delocalized π -electron system between the 1,4-bismethylium-benzene ring and two 3-guaiazulenyl groups. The molecular formula C₃₈H₄₀ for the dicarbenium unit was determined by the exact FAB-MS spectrum (Found: m/z 496.3146; Calcd for C₃₈H₄₀: [M-2PF₆]⁺, m/z 496.3130). The elemental analysis confirmed the molecular formula C₃₈H₄₀P₂F₁₂ (Found: H, 4.66; C, 51.05%. Calcd for C₇₆H₈₉O₄P₅F₃₀ [2(C₃₈H₄₀P₂F₁₂)]



$\text{HPF}_6 \cdot 4\text{H}_2\text{O}$): H, 5.01; C, 50.96%). The 500 MHz ^1H -NMR (CD_3CN) spectrum showed signals for two symmetric 3-guaiazulenyl groups at δ 1.50(12H, d, J =7.0 Hz, $(\text{CH}_3)_2\text{CH}$ -7',7''), 2.57(6H, s, Me-1',1''), 3.42(6H, s, Me-4',4''), 3.55(2H, sept, J =7.0 Hz, $(\text{CH}_3)_2\text{CH}$ -7',7''), 8.49(2H, brd, J =11.0 Hz, H-5',5''), 8.61(2H, brd, J =11.0 Hz, H-6',6''), 8.63(2H, brs, H-8',8''), 8.81(2H, brs, H-2',2'')⁸ and an overlapping signal for 1,4-bismethylumbenzene ring at δ 8.03(6H, brs, H-2,3,5,6 and CH-1,4). The 125 MHz ^{13}C -NMR (CD_3CN) spectrum exhibited the following seventeen carbon signals: δ 173.1, 162.2, 158.6, 153.9, 151.6(C-6',6''), 148.2(C-2',2''), 147.5, 145.6(C-5',5''), 142.2, 141.0(CH-1,4), 140.2(C-8',8''), 139.4, 134.2(C-2,3,5,6), 40.5($(\text{CH}_3)_2\text{CH}$ -7',7''), 29.9(Me-4',4''), 23.8($(\text{CH}_3)_2\text{CH}$ -7',7''), and 14.1(Me-1',1''). These spectroscopic data and the elemental analysis led to the structure 1,4-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate for compound **3**. In the previous paper,⁹ we reported that the reaction of guaiazulene (**1**) with a 0.25 molar amount of terephthalaldehyde in acetic acid not containing hydrochloric acid at 25 °C for 4 h under argon quantitatively gave 4-[di(3-guaiazulenylmethyl)]benzaldehyde; however, no 1,4-bis[di(3-guaiazulenylmethyl)]benzene was obtained. Therefore, it was found that the presence of hydrochloric acid under the above reaction conditions played an important role to yield the 1,4-bis(3-guaiazulenylmethylium)benzene structure. The electrochemical behavior of compound **3** was then measured by means of CV and DPV in 0.1 M Et_4NClO_4 , CH_3CN (Figure 2). Four redox

potentials observed by DPV were positioned at the E_p values of +0.04, -0.24, -1.55, and -1.80V, while the corresponding four irreversible and one reversible redox potentials determined by CV were located at the values of +0.58(E_{pa}), +0.01(E_{pc}), -0.29(E_{pc}), -1.55(E_{pc}), and -1.83V($E_{1/2}$).¹⁰ The redox potentials thus obtained for **3** indicate that the two guaiazulenyl groups of **3** are susceptible to oxidation and less susceptible to reduction as compared with guaiazulene (**1**)¹¹ (Figure 2) and **3** is further stepwise reduced at the electroreduction potentials [-0.24(E_{red}^1) and -1.55(E_{red}^2)]. Furthermore, it should be noticed that the absorption maximum (λ_{max} 507 nm) of compound **3** is close to the maximum wavelength of the solar spectrum. Thus, the basic studies on generation of physical and chemical functions by using compound **3** are of interest from a viewpoint of potential utility of functional delocalized π -electron system such as photosensitive dyes, and are currently under intensive investigation.

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References and Notes

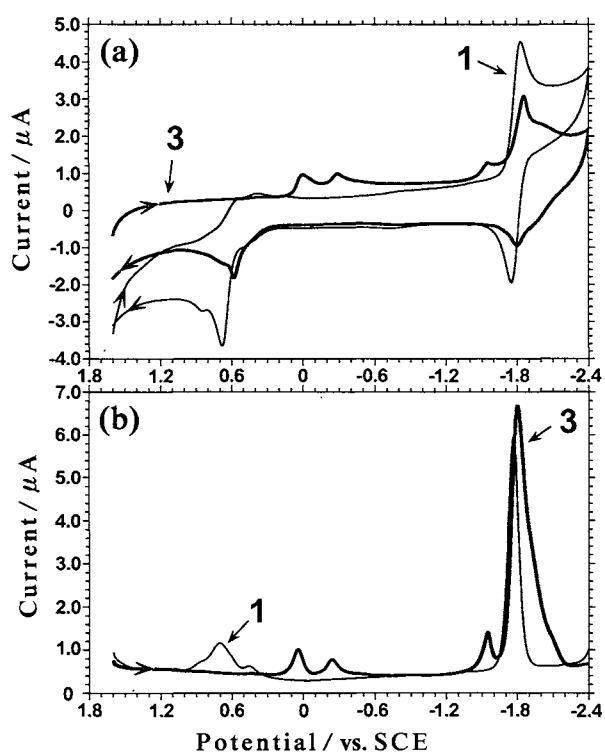


Figure 2. Cyclic (a) and differential pulse (b) voltammograms of compounds **1** (2.0 mg, 10.1 μmol) and **3** (4.0 mg, 5.2 μmol) dissolved in 0.1 M Et_4NClO_4 , CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s⁻¹ at 25 °C under argon, respectively.

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- Partly presented at the 76th Meeting of Japan Chemical Society, Kanagawa, March 1999, Abstr. No. 3 PB 060 (p. 1441).
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- The structure of 1,4-bis(3-guaiazulenylmethylium)benzene dichloride for **2**, reddish-orange paste, is based on the following spectral data: UV-visible λ_{max} (CH_3COOH) nm (log ϵ), 267(4.94), 282sh(4.85), 304sh(4.70), 328sh(4.66), 377(4.73), 461(4.78), and 527sh(4.70); exact FAB-MS (Found: m/z 496.3109; Calcd for $\text{C}_{38}\text{H}_{40}$: $[\text{M}-2\text{Cl}]^+$, m/z 496.3130). The 500 MHz ^1H -NMR (CD_3COOD) spectrum showed signals for two symmetric 3-guaiazulenyl groups at δ 1.51(12H, d, J =7.0 Hz, $(\text{CH}_3)_2\text{CH}$ -7',7''), 2.61(6H, s, Me-1',1''), 3.52(6H, s, Me-4',4''), 3.58(2H, sept, J =7.0 Hz, $(\text{CH}_3)_2\text{CH}$ -7',7''), 8.57(2H, brd, J =11.0 Hz, H-5',5''), 8.68(2H, brs, H-8',8''), 8.75(2H, brd, J =11.0 Hz, H-6',6''), and 8.94(2H, brs, H-2',2'') and an overlapping signal for 1,4-bismethylumbenzene ring at δ 8.14(6H, brs, H-2,3,5,6 and CH-1,4). The 125 MHz ^{13}C -NMR (CD_3COOD): δ 172.9, 162.2, 158.8, 154.0, 151.9(C-6',6''), 148.5(C-2',2''), 147.4, 145.4(C-5',5''), 142.2, 141.3(CH-1,4), 139.6(C-8',8''), 134.5(C-2,3,5,6), 40.6($(\text{CH}_3)_2\text{CH}$ -7',7''), 30.0(Me-4',4''), 24.0($(\text{CH}_3)_2\text{CH}$ -7',7''), and 14.1(Me-1',1'').
- The chemical shifts (δ ppm) of H-2' and 2" protons for **3** are appreciably downfield shifted as compared with those of 1,4-bis(diaza- C_6H_4 -methylium)benzene bishexafluorophosphates,^{6a} indicating that those protons of **3** exist on the coplanar as the 1,4-bismethylium carbons, respectively.
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- For a comparative purpose, the oxidation potential (E/V vs. SCE) using ferrocene as a standard material showed +0.43 V by DPV and +0.44 V by CV under the same electrochemical conditions as those for compound **3**.
- 1, DPV (E_p value): +0.70 and -1.77 V; CV ($E_{1/2}$ value): +0.68 (E_{pa}) and -1.79 V.