

## Preparation and Characteristic Properties of 1,4-Bis(3-guaiazulenylmethylum)benzene Bishexafluorophosphate

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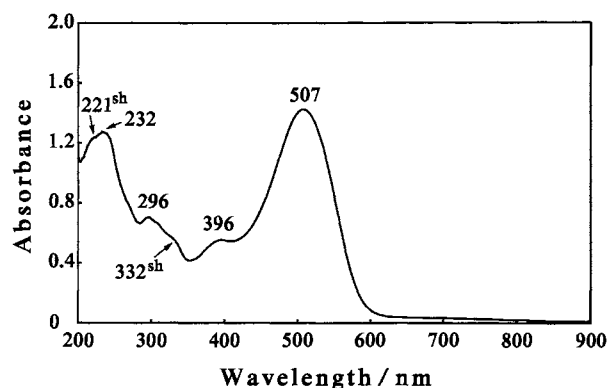
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Reaction of guaiazulene (**1**) with a 0.5 molar amount of terephthalaldehyde in acetic acid in the presence of hydrochloric acid at 25 °C for 10 min under aerobic conditions selectively affords 1,4-bis(3-guaiazulenylmethylum)benzene dichloride (**2**),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

As a series of basic studies on the creation of novel functional materials with delocalized  $\pi$ -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.<sup>1</sup> 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 dicarbocation compound, 1,4-bis(3-guaiazulenylmethylum)benzene dichloride (**2**), which upon treatment with hexafluorophosphoric acid quantitatively forms the title bishexafluorophosphate **3** as stable crystals.<sup>2</sup> It is expected that compound **3** is converted into 7,8-di(3-guaiazulenyl)-*p*-quinodimethane.<sup>3</sup> 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-benzylideneguaiazulenium salts,<sup>4</sup> and which were further converted into the corresponding diazulenylmethanes, respectively.<sup>5</sup> In addition, Asao and his co-workers reported synthesis and characteristic properties (e.g.,  $pK_R^+$  values) of several mono-, di- and tricarboxylates stabilized by azulene rings in detail.<sup>6</sup> We wish to describe herein a facile preparation and characteristic properties of novel dicarbocation compounds **2** and **3** obtained from naturally occurring guaiazulene, which enabled us to compare with the characteristic properties of the dicarbocation compounds, 1,3- and 1,4-bis(diazulenylmethylum)benzene bishexafluorophosphates.<sup>6a</sup>

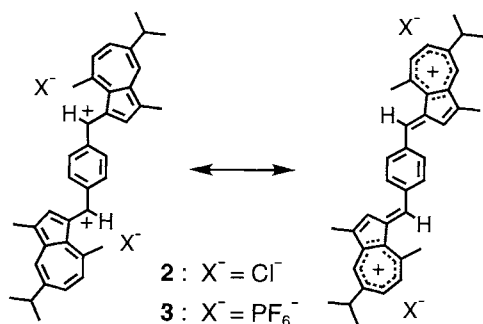


**Figure 1.** The UV-visible spectrum of compound **3** in CH<sub>3</sub>CN. Concentration, 0.022 g/L; length of the cell, 1 cm.

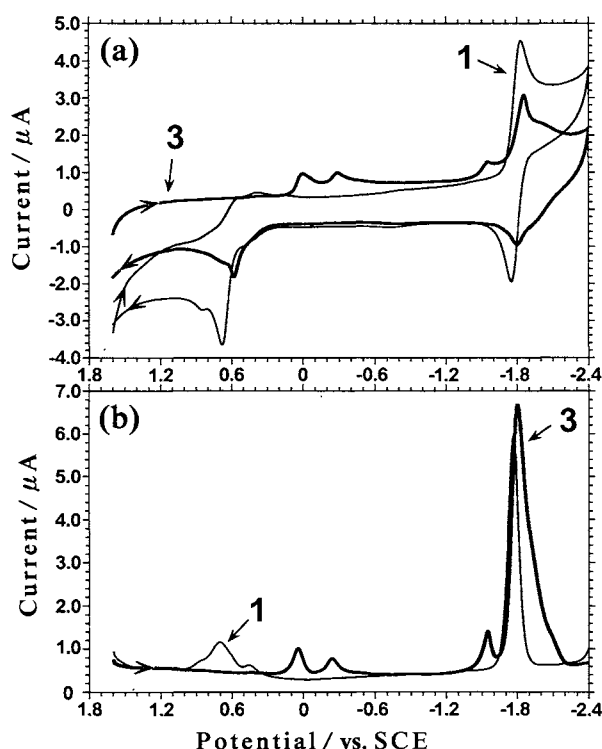
lium)benzene bishexafluorophosphates.<sup>6a</sup>

1,4-Bis(3-guaiazulenylmethylum)benzene bishexafluorophosphate (**3**) was prepared by the following procedures: To a solution of guaiazulene (**1**) (12 mg, 61  $\mu$ mol) dissolved in acetic acid (0.5 mL) was added a solution of terephthalaldehyde (4 mg, 30  $\mu$ mol) dissolved in acetic acid (0.5 mL) containing hydrochloric acid (35% aqueous solution, 45  $\mu$ L). The mixture was stirred at 25 °C for 10 min under aerobic conditions, giving 1,4-bis(3-guaiazulenylmethylum)benzene dichloride (**2**)<sup>7</sup> as a sole product. Addition of hexafluorophosphoric acid (60% aqueous solution, 100  $\mu$ 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, <sup>1</sup>H- and <sup>13</sup>C-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:  $\lambda$  max (CH<sub>3</sub>CN) nm (log  $\epsilon$ ), 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  $\pi$ -electron system between the 1,4-bismethylum-benzene ring and two 3-guaiazulenyl groups. The molecular formula C<sub>38</sub>H<sub>40</sub> for the dicarbocation unit was determined by the exact FAB-MS spectrum (Found:  $m/z$  496.3146; Calcd for C<sub>38</sub>H<sub>40</sub>: [M-2PF<sub>6</sub>]<sup>+</sup>,  $m/z$  496.3130). The elemental analysis confirmed the molecular formula C<sub>38</sub>H<sub>40</sub>P<sub>2</sub>F<sub>12</sub> (Found: H, 4.66; C, 51.05%. Calcd for C<sub>76</sub>H<sub>80</sub>O<sub>4</sub>P<sub>5</sub>F<sub>30</sub> [2(C<sub>38</sub>H<sub>40</sub>P<sub>2</sub>F<sub>12</sub>) ·



HPF<sub>6</sub>·4H<sub>2</sub>O]: H, 5.01; C, 50.96%). The 500 MHz <sup>1</sup>H-NMR (CD<sub>3</sub>CN) spectrum showed signals for two symmetric 3-guaiazulenyl groups at  $\delta$  1.50(12H, d,  $J=7.0$  Hz, (CH<sub>3</sub>)<sub>2</sub>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, (CH<sub>3</sub>)<sub>2</sub>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'')<sup>8</sup> and an overlapping signal for 1,4-bismethylumbenzene ring at  $\delta$  8.03(6H, brs, H-2,3,5,6 and CH-1,4). The 125 MHz <sup>13</sup>C-NMR (CD<sub>3</sub>CN) spectrum exhibited the following seventeen carbon signals:  $\delta$  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((CH<sub>3</sub>)<sub>2</sub>CH-7',7''), 29.9(Me-4',4''), 23.8((CH<sub>3</sub>)<sub>2</sub>CH-7',7''), and 14.1(Me-1',1''). These spectroscopic data and the elemental analysis led to the structure 1,4-bis(3-guaiazulenylmethyl)benzene bishexafluorophosphate for compound **3**. In the previous paper,<sup>9</sup> 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-guaiazulenyl)methyl]benzaldehyde; however, no 1,4-bis[di(3-guaiazulenyl)methyl]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-guaiazulenylmethyl)benzene structure. The electrochemical behavior of compound **3** was then measured by means of CV and DPV in 0.1 M Et<sub>4</sub>NClO<sub>4</sub>, CH<sub>3</sub>CN (Figure 2). Four redox



**Figure 2.** Cyclic (a) and differential pulse (b) voltammograms of compounds **1** (2.0 mg, 10.1  $\mu$ mol) and **3** (4.0 mg, 5.2  $\mu$ mol) dissolved in 0.1 M Et<sub>4</sub>NClO<sub>4</sub>, CH<sub>3</sub>CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s<sup>-1</sup> at 25 °C under argon, respectively.

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( $E_{1/2}$ ).<sup>10</sup> 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**)<sup>11</sup> (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 ( $\lambda_{max}$  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  $\pi$ -electron system such as photosensitive dyes, and are currently under intensive investigation.

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## References and Notes

- Partly presented at the 28th Symposium on Structural Organic Chemistry, Hiroshima, November 1998, Abstr. No. 3P49 (p. 327).
- Partly presented at the 76th Meeting of Japan Chemical Society, Kanagawa, March 1999, Abstr. No. 3 PB 060 (p. 1441).
- The reaction conditions are currently under intensive investigation.
- D. H. Reid, W. H. Stafford, W. L. Stafford, G. McLennan, and A. Voigt, *J. Chem. Soc.*, **1958**, 1110.
- V. H. Franke and M. Mühlstädt, *J. Praktische Chem.*, **35**, 262 (1967).
- a) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **33**, 3773 (1992). b) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **35**, 751 (1994). c) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **35**, 755 (1994). d) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **35**, 3723 (1994). e) S. Ito, N. Morita, and T. Asao, *Chem. Lett.*, **1994**, 477. f) S. Ito, M. Fujita, N. Morita, and T. Asao, *Chem. Lett.*, **1995**, 475. g) S. Ito, M. Fujita, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 3611 (1995). h) S. Ito, S. Kikuchi, N. Morita, and T. Asao, *Chem. Lett.*, **1996**, 175. i) S. Ito, N. Morita, and T. Asao, *J. Org. Chem.*, **61**, 5077 (1996).
- The structure of 1,4-bis(3-guaiazulenylmethyl)benzene dichloride for **2**, reddish-orange paste, is based on the following spectral data. UV-visible  $\lambda_{max}$  (CH<sub>3</sub>COOH) nm (log  $\epsilon$ ), 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 C<sub>38</sub>H<sub>40</sub>: [M-2Cl]<sup>+</sup>,  $m/z$  496.3130). The 500 MHz <sup>1</sup>H-NMR (CD<sub>3</sub>COOD) spectrum showed signals for two symmetric 3-guaiazulenyl groups at  $\delta$  1.51(12H, d,  $J=7.0$  Hz, (CH<sub>3</sub>)<sub>2</sub>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, (CH<sub>3</sub>)<sub>2</sub>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  $\delta$  8.14(6H, brs, H-2,3,5,6 and CH-1,4). The 125 MHz <sup>13</sup>C-NMR (CD<sub>3</sub>COOD):  $\delta$  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((CH<sub>3</sub>)<sub>2</sub>CH-7',7''), 30.0(Me-4',4''), 24.0((CH<sub>3</sub>)<sub>2</sub>CH-7',7''), and 14.1(Me-1',1'').
- The chemical shifts ( $\delta$  ppm) of H-2' and 2'' protons for **3** are appreciably downfield shifted as compared with those of 1,4-bis(diazaulenylmethyl)benzene bishexafluorophosphates,<sup>6a</sup> indicating that those protons of **3** exist on the coplanar as the 1,4-bismethylumbenzene carbons, respectively.
- S. Takekuma, H. Takekuma, Y. Hatanaka, J. Kawaguchi, and H. Yamamoto, *Nippon Kagaku Kaishi*, **1998**, 275.
- 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.