An efficient preparation and the properties of 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate

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Abstract—Reaction of guaiazulene (**1**) with a 0.5 molar amount of phthalaldehyde in acetic acid in the presence of hexafluorophosphoric acid at 25°C for 2 h under aerobic conditions quantitatively gives the title new dicarbocation compound, 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate (**3**), which upon reduction with zinc powder in acetonitrile at 0°C under aerobic conditions rapidly affords a unique rearrangement product, 6,11-dimethyl-12-(3-guaiazulenyl)-9-isopropylnaphtho[2,3-a]azulene (**5**), as a major product. © 2001 Elsevier Science Ltd. All rights reserved.

In a previous paper,[1] we reported an efficient preparation and the characteristic properties of a unique dicarbocation compound, 1,4-bis(3-guaiazulenylmethylium)-benzene bishexafluorophosphate (**2**), which upon reduction with zinc powder in acetonitrile at 0°C under argon afforded the corresponding 7,8-bis(3-guaiazulenyl)-*p*-quinodimethane that was a reactive substance under aerobic conditions.[2] Our interest has been focused on the characteristic and chemical properties of the position isomer of **2**, 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate (**3**), with a view to comparison and discussion with those of **2**. We

now wish to report the detailed studies on a one-pot synthesis, the structure, and the characteristic and chemical properties of **3** possessing larger steric hindrance and repulsion between the two adjacent 3-guaiazulenylmethylium substituents and the benzene ring in comparison with the molecular structure of **2**.

Compound **3** was prepared according to the procedure shown in Ref. 3: **3** (88% isolated yield) was dark-orange needles, mp>120°C [decomp, determined by thermal analysis (TGA and DTA)]. The UV–vis spectrum is shown in Fig. 1: λ_{max} (CH$_3$CN) nm (log ε), 222sh(4.70), 236(4.72), 287(4.56), 326sh(4.41), 368(4.46), 440(4.45) and 466sh(4.44). Similarly as in the case of **2**, no characteristic absorption bands for guaiazulene were observed, indicating formation of a charge transfer (CT) complex between the 1,2-bis(3-guaiazulenylmethylium)benzene moiety and the bishexafluorophosphate. The absorption maximum appeared at λ_{max} 440 nm, which showed a larger hypsochromic shift (71 nm) and hypochromic effect in comparison with that of **2**[4] (λ_{max} 511 nm, log ε=4.87) (Fig. 1), suggesting it to be an *intra*-molecular CT band. Moreover, the reason why the larger hypsochromic shift and hypochromic effect can be inferred is that **3** can not π-conjugate between the two adjacent 3-guaiazulenylmethylium ions and the benzene ring owing to influence of the steric hindrance and repulsion between them. The IR (KBr) spectrum showed the two specific bands based on the counter anion (PF$_6^-$) at ν_{max} 837 and 556 cm^{-1}, which coincided with those of **2**.[4] The MALDI-TOF-MS spectrum [2-(4-hydroxyphenylazo)benzoic acid matrix] showed the ion
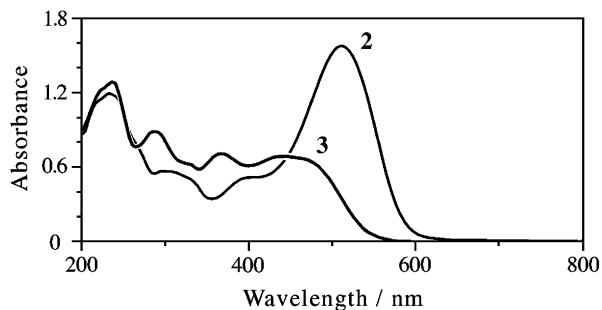

Figure 1. The UV–vis spectra of compounds **2**[4] and **3** in CH$_3$CN. Concentrations, **2** and **3**: 0.020 g/L each; length of the cell, 1 cm.

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peaks at m/z 315(100%), 496([M−2PF$_6$]$^+$, 60), 641([M−PF$_6$]$^+$, 90) and 694([M−2PF$_6$+1]$^+$, 30). The molecular formula C$_{38}$H$_{40}$ for the dicarbocation unit was determined by the exact FAB-MS spectrum (3-nitrobenzyl alcohol matrix; Found: m/z 496.3174; Calcd for C$_{38}$H$_{40}$: [M−2PF$_6$]$^+$, m/z 496.3130). The elemental analysis confirmed the molecular formula C$_{38}$H$_{40}$F$_{12}$P$_2$ [Found: H, 5.70; C, 55.50%. Calcd for C$_{38}$H$_{44}$O$_2$F$_{12}$P$_2$ (C$_{38}$H$_{40}$·2PF$_6$·2H$_2$O): H, 5.39; C, 55.48%.]. The 500 MHz ^{1}H NMR (CD$_3$CN) spectrum showed signals, indicating that the two 3-guaiazulenyl groups are equivalent, at δ 1.45(12H, d, J=7.0 Hz, (CH$_3$)$_2$CH-7′,7″), 2.42(6H, brd s, Me-1′,1″), 3.23(6H, s, Me-4′,4″), 3.50(2H, sept, J=7.0 Hz, Me$_2$CH-7′,7″), 8.45(2H, dd, J=11.0, 2.0 Hz, H-6′,6″), 8.54(2H, d, J=11.0 Hz, H-5′,5″), 8.55(2H, d, J=2.0 Hz, H-8′,8″), 8.79(2H, brd s, H-2′,2″) and signals for the 1,2-bismethyliumbenzene unit at δ 7.66(2H, brd s, HC$^+$-1,2) and 7.80(4H, s, H-3,4,5,6). The 125 MHz ^{13}C NMR (CD$_3$CN) spectrum exhibited the following 18 carbon signals assigned by the ^{1}H–^{13}C COSY and ^{1}H–^{13}C COLOC techniques: δ 173.8(C-7′,7″), 163.0(C-1′,1″), 158.8(C-4′,4″), 153.3(C-3a′,3a″), 152.0(C-5′,5″), 147.5(C-2′,2″), 147.3(C-8a′,8a″), 145.7(C-6′,6″), 143.3(C-3′,3″), 141.4(HC$^+$-1,2), 140.2(C-8′,8″), 138.0(C-1,2), 134.2(C-3,6), 132.3(C-4,5), 40.6(Me$_2$CH-7′,7″), 29.6(Me-4′,4″), 23.8((CH$_3$)$_2$CH-7′,7″) and 13.8(Me-1′,1″). Therefore, the up-field shifts ($\Delta\delta$ ppm) for the proton signals of Me-1′,1″ (−0.15), Me-4′,4″ (−0.19), HC$^+$-1,2 (−0.37) and H-3,4,5,6 (−0.23), the down- and up-field shifts ($\Delta\delta$ ppm) for the carbon signals of C-3′,3″ (+1.1) and C-1,2 (−1.4) respectively adjacent to the HC$^+$-1,2 carbonium ions were observed in comparison with those of **2**[1] by influence of the ring currents on the two adjacent 3-guaiazulenylmethylium ions and the benzene ring. These spectroscopic data and the elemental analysis led to the structure, 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate for **3**. Although an X-ray crystal structure of **3** has not yet been achieved because of difficulty in obtaining a single crystal suitable for this purpose, the optimized structure for the dicarbocation unit, 1,2-bis(3-guaiazulenylmethylium)benzene, has been calculated by a WinMOPAC program using a semiempirical Hamiltonian (AM1).[5] As a result, it is presumed that the two 3-guaiazulenylmethylium planes of **3** symmetrically twist by 57.8° from the benzene ring (symmetry: C_2, the distance between HC$^+$-1 and HC$^+$-2

carbon atoms: 2.936 Å) owing to influence of the steric hindrance between them, the repulsion between the two 3-guaiazulenylmethylium ions, and so on (Fig. 2), indicating that it can not π-conjugate between the two adjacent 3-guaiazulenylmethylium ions and the benzene ring. The UV–vis and NMR spectral data of **3** compared with those of **2** also bear out the above optimized structure.

We have been interested further in a comparative study of the electrochemical properties of **2**[1,4] and **3**. The electrochemical behavior of **3** was, therefore, measured by means of CV and DPV (Potential/V versus SCE) in 0.1 M [n-Bu$_4$N]PF$_6$, CH$_3$CN (Fig. 3).[6] Six redox potentials observed by DPV were positioned at the E_p values of +0.05, −0.30, −1.59, −1.81, −1.89 and −2.27 V, while the redox potentials determined by CV were located at the values of +0.84(E_{pa}), +0.62(E_{pa}), −0.02(E_{pc}), −0.33($E_{1/2}$), −1.63($E_{1/2}$), −1.87($E_{1/2}$) and −2.31(E_{pc}) V. From a comparative study with the redox potentials of **1**,[7] **2**[4] and the monocarbocation compound, 1-isopropyl-4-(3-guaiazulenylmethylium)benzene hexafluorophosphate (**4**),[2,8] it can be inferred that: (1) **3** stepwise undergoes two-electron reduction at the potentials of −0.02(E_{pc}) and −0.33($E_{1/2}$) V by CV (corresponding to +0.05 and −0.30 V by DPV), suggesting it is converted into 7,8-bis(3-guaiazulenyl)-o-quinodimethane via the corresponding biradical, which is presumed to be too reactive to be isolated; (2) 7,8-bis(3-guaiazulenyl)-o-quinodimethane yielded is further reduced to the tetraanion at the potentials of −1.59, −1.81, −1.89 and −2.27 V by DPV [corresponding to −1.63($E_{1/2}$), −1.87($E_{1/2}$) (overlapping two reduction potentials) and −2.31(E_{pc}) V by CV]; and further, (3) along with the four-electron reduction, 7,8-bis(3-guaiazulenyl)-o-quinodimethane, stepwise undergoes two-electron oxidation at the potentials of +0.62(E_{pa}) and +0.84(E_{pa}) by CV, suggesting it is converted into the starting 1,2-bis(3-guaiazulenylmethylium)benzene. Thus, the reason why the reduction potential (E_{pc}: −0.02 V) observed by CV was positioned at the E_p value of +0.05 V by DPV can be assumed to be due to the structural conversion from the o-quinodimethane to the 1,2-bis(3-guaiazulenylmethylium)benzene.

In addition to the above investigations, we studied the chemical property of **3**, and have found that the reduc-
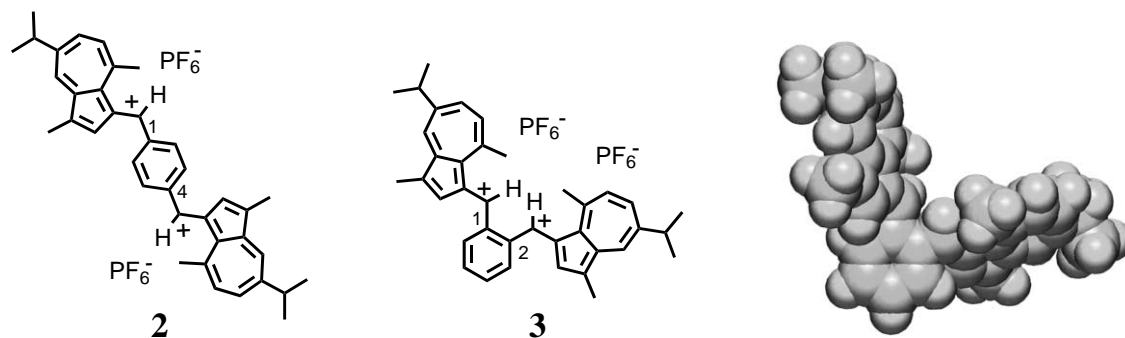

Figure 2. Structures of the products **2**,[1,4] **3** and the optimized space-filling structure for the dicarbocation, 1,2-bis(3-guaiazulenylmethylium)benzene unit of **3** calculated by a WinMOPAC program.[5]
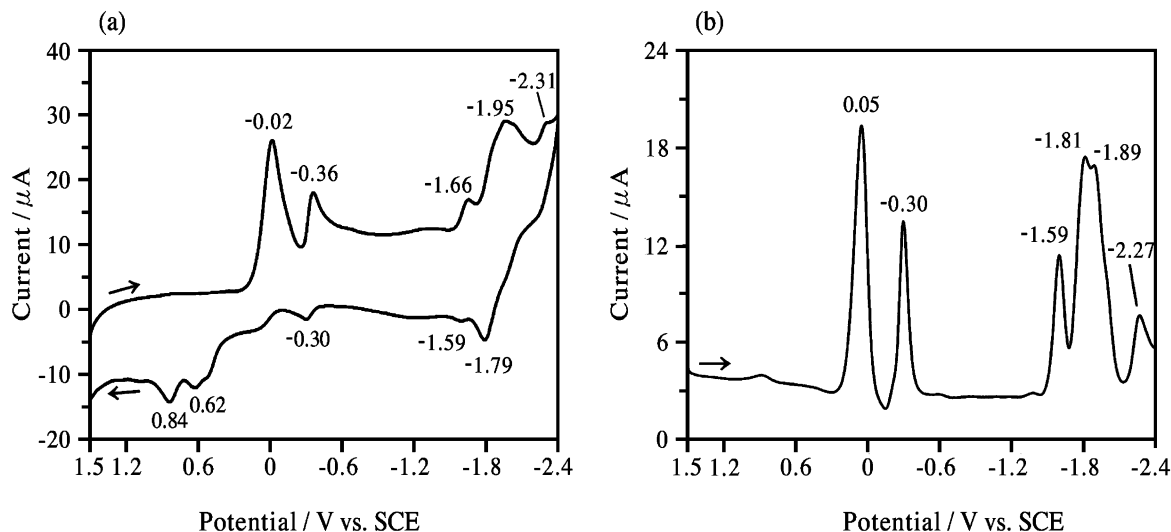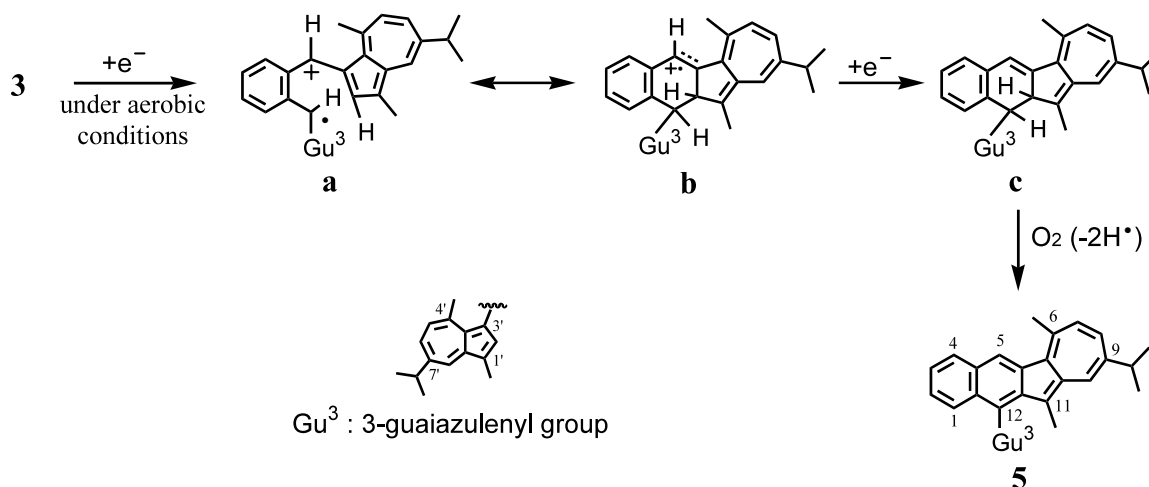
Figure 3. Cyclic (a) and differential pulse (b) voltammograms of compound **3** (6.0 mg, 7.3 μmol) in 0.1 M [n-Bu$_4$N]PF$_6$, CH$_3$CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25°C under argon, respectively.

Scheme 1. A plausible reaction pathway for the formation of compound **5**.

tion of **3** with zinc powder in acetonitrile at 0°C under aerobic conditions rapidly afforded a unique rearrangement product, 6,11-dimethyl-12-(3-guaiazulenyl)-9-isopropylnaphtho[2,3-*a*]azulene (**5**) as a major product (11% isolated yield),[9] whose structure was established on the basis of the spectroscopic data [UV–vis, EI-MS (including its exact MS) and NMR (500 MHz for ^{1}H)].[10] A plausible reaction pathway for the formation of **5** based on the electrochemical behavior of **3** is illustrated in Scheme 1; namely, **3** undergoes one-electron reduction, leading to the formation of **b** owing to the *intra*-molecular cycloaddition of the cation-radical **a** generated, which is further reduced to the intermediate **c**. The **c** yielded is rapidly converted into compound **5** under aerobic conditions. Along with the chemistry of naphtho[2,3-*a*]azulenes which has been studied to a considerable extent and the documented chemical and electrochemical properties for those compounds,[11] the present work can be expected to provide valuable information on potential synthetic application to the preparation of some naphtho[2,3-*a*]azulenes. Thus, the facile preparative method of **5** enables us to investigate more properties of naphtho[2,3-*a*]azulenes in detail.

References

1. Takekuma, S.; Sasaki, M.; Takekuma, H.; Yamamoto, H. *Chem. Lett.* **1999**, 999–1000.
2. Details will be reported elsewhere.

3. Compound **3** was prepared by the following procedure: To a solution of guaiazulene (**1**) (90 mg, 0.45 mmol) in acetic acid (0.4 mL) was added a solution of phthalaldehyde (30 mg, 0.22 mmol) in acetic acid (0.2 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.24 mL). The mixture was stirred at 25°C for 2 h under aerobic conditions, giving a precipitation of a dark-orange solid of **3**. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:2, vol/vol) to provide pure **3** as stable crystals (152 mg, 88% yield).

4. The previously obtained **2**[1] was recrystallized from acetonitrile–diethyl ether (1:2, vol/vol) to provide more pure **2** as dark-red prisms: The elemental analysis confirmed the molecular formula $C_{38}H_{40}F_{12}P_2$ (Found: H, 4.91; C, 55.85%. Calcd for $C_{152}H_{161}F_{54}P_9$ [4($C_{38}H_{40}\cdot2PF_6$)·HPF_6]: H, 4.93; C, 55.45%.); UV–vis λ_{max} (CH_3CN) nm (log ε), 215sh(4.71), 231(4.74), 270sh(4.53), 295(4.42), 328sh(4.37), 388sh(4.36) and 511(4.87); IR (KBr), ν_{max} 841 and 559 cm^{-1} (PF_6^-); DPV (E_p): +0.04, −0.25, −1.63 and −1.87 V; CV: +0.64(E_{pa}), −0.02(E_{pc}), −0.29(E_{pc}), −1.67(E_{pc}), −1.89(E_{pc}), −2.07sh(E_{pc}) and −1.84(E_{pa}) V.

5. The MO calculation program (Ver. 2.0) was developed by Fujitsu Ltd., Japan. The following calculation conditions [i.e., semiempirical Hamiltonian (AM1) and keywords (CHARGE = +2, LET, ALLVEC, VECTORS, BONDS, EF, GEO-OK, PL, GRADIENTS, SCFCRT = 10^{-10}, T = 10 D, PRECISE and GNORM = 10^{-8})] were used. The final value for the Gradient Norm of the optimized structure showed 0.017536.

6. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42(E_p) V by DPV and +0.40($E_{1/2}$) V by CV under the same electrochemical conditions as **3**.

7. **1**, DPV (E_p): +0.59 and −1.77 V; CV: +0.69(E_{pa}) and −1.83($E_{1/2}$) V.

8. **4**, DPV (E_p): −0.22, −1.80 and −1.94sh V; CV: + 0.65(E_{pa}), −0.29(E_{pc}), −1.85($E_{1/2}$) and −1.99(E_{pc}) V.[2]

9. Although TLC monitoring of the reaction products obviously indicated its formation in a much larger proportion, compound **5** was isolable in 11% yield apparently because of its instability during the repeated purification. The purification method isolating a larger amount of **5** and structures of other minor products are currently under intensive investigation.

10. Compound **5** was prepared according to the following method: Reduction of **3** (60 mg, 72 μmol) with zinc powder (20 mg, 0.31 mmol) in acetonitrile (1 mL) at 0°C for 10 min under aerobic conditions gave **5** (4 mg, 11% yield; conversion: 100%), which was isolated by careful chromatographic purification. **5**: Dark-green prisms (from MeOH), mp>120°C [decomp, determined by the thermal analysis (TGA and DTA)]; R_f = 0.63 on silica-gel TLC (hexane–benzene–AcOEt = 6/3/1, vol/vol/vol); UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 245(4.44), 293(4.62), 308(4.51), 322sh(4.44), 355sh(4.02), 368sh(3.93), 402sh(3.66), 426(3.66), 452sh(3.51), 546sh(2.60), 615(2.72), 672sh(2.64) and 744sh(2.31); EI-MS m/z 494(M$^+$, 100%) [Found: m/z 494.2964. Calcd for $C_{38}H_{38}$: M$^+$, 494.2973.]; ^{1}H NMR (CD_2Cl_2), δ 1.20(6H, brd d, J = 7.0 Hz, (C$\underline{H}_3$)$_2$CH-9), 1.42(3H, d, J = 7.0 Hz, (C$\underline{H}_3$)$_2$CH-7′), 1.43(3H, d, J = 7.0 Hz, (C$\underline{H}_3$)$_2$CH-7′), 1.54(3H, s, Me-4′), 1.93(3H, s, Me-11), 2.69(1H, sept, J = 7.0 Hz, (CH$_3$)$_2$C$\underline{H}$-9), 2.76(3H, s, Me-1′), 3.03(3H, s, Me-6), 3.13(1H, sept, J = 7.0 Hz, (CH$_3$)$_2$C$\underline{H}$-7′), 6.53(1H, dd, J = 12.0, 1.6 Hz, H-8), 6.58(1H, d, J = 12.0 Hz, H-7), 6.79(1H, d, J = 10.5 Hz, H-5′), 7.20(1H, brd d, J = 1.6 Hz, H-10), 7.30(1H, brd d, J = 8.0 Hz, H-4), 7.34(1H, ddd, J = 6.0, 8.0, 1.0 Hz, H-3), 7.36(1H, dd, J = 10.5, 2.0 Hz, H-6′), 7.44(1H, ddd, J = 8.0, 6.0, 1.5 Hz, H-2), 7.50(1H, brd s, H-2′), 8.17(1H, brd d, J = 8.0 Hz, H-1), 8.33(1H, d, J = 2.0 Hz, H-8′) and 8.89(1H, brd s, H-5).

11. (a) Yasunami, M.; Yang, P. W.; Kondo, Y.; Noro, Y.; Takase, K. *Chem. Lett.* **1980**, 167–170; (b) Bindl, J.; Pilidis, G.; Daub, J. *Angew. Chem.* **1984**, *96*, 294–296; (c) Bindl, J.; Burgemeister, T.; Daub, J. *Chem. Ber.* **1985**, *118*, 4934–4945; (d) Seitz, U.; Daub, J. *Synthesis* **1986**, 686–689; (e) Bindl, J.; Seitz, P.; Seitz, U.; Salbeck, E.; Salbeck, J.; Daub, J. *Chem. Ber.* **1987**, *120*, 1747–1756; (f) Salbeck, J.; Daub, J. *Chem. Ber.* **1989**, *122*, 1681–1690.