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The Facile Preparation, Crystal Structure, and Chemical and Electrochemical Properties of 9-Anthryl-3-guaiazulenylmethylium Hexafluorophosphate

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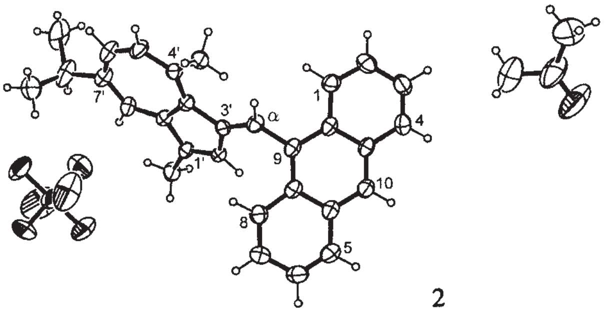
Reaction of guaiazulene (**1**) with anthracene-9-carbaldehyde in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min gave the title compound **2** in 88% yield.

In previous papers, we reported a facile preparation, crystal structures, the spectroscopic and characteristic chemical properties, and, further, the electrochemical behavior of mono- and dicarbocations stabilized by a 3-guaiazulenyl group.[1–3] As a series of basic studies on the creation of novel functional materials with naturally occurring guaiazulene (**1**) and their potential utility, our interest has recently been focused on the title investigations of a new monocarbocation compound, 9-anthryl-3-guaiazulenylmethylium hexafluorophosphate (**2**), possessing larger steric hindrance and repulsion between the 3-guaiazulenylmethylium substituent and the 9-anthryl group in comparison with the molecular structure of 3-guaiazulenyl(phenyl)methylium hexafluorophosphate (and tetrafluoroborate) (**3a** and **3b**).[1–3]

Compound **2** was prepared by the following procedure. To a solution of **1** (100 mg, 0.50 mmol) in methanol (1 mL) was added a solution of anthracene-9-carbaldehyde (156 mg, 0.76 mmol) in methanol (2 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25 °C for 30 min under aerobic conditions to give a dark-blue solid, **2**. The thus-obtained crude product was carefully washed with diethyl ether and recrystallized from acetone–hexane (1:5, v/v) to provide pure **2** as stable crystals with an equimolar amount of acetone (261 mg, 88% yield). Instrumental analyses of **2** were carried out according to procedures described before.[1–3] A characteristic vis absorption band based on the formation of the 9-anthryl-3-guaiazulenylmethylium moiety with a delocalized π-electron system appeared at the absorption maximum (λ_{max} 588 nm, $\log \varepsilon = 3.97$), which showed larger bathochromic shift in comparison with that of **3a** (λ_{max} 456 nm, $\log \varepsilon = 4.30$).[2] The chemical shifts (δ, ppm) for the proton and carbon signals of the HC$^+$-α carbenium-ion center of **2** (9.46 for ^{1}H NMR; 148.2 for ^{13}C NMR) in acetonitrile-d_3 showed down- and up-field shifts, respectively, in comparison with those of the HC$^+$-α carbenium-ion center of **3a** (8.78 for ^{1}H NMR; 149.6 for ^{13}C NMR)[2,3] in acetonitrile-d_3. The elemental analysis and the spectroscopic data for **2**[4] led to the molecular structure, 9-anthryl-3-guaiazulenylmethylium hexafluorophosphate, with a delocalized π-electron system.



2

Fig. 1. The ORTEP drawing of **2**[5] with an equimolar amount of acetone (30% probability thermal ellipsoids).

The crystal structure of **2** was determined by means of X-ray diffraction, producing accurate structural parameters.[5] The ORTEP drawing of **2**, indicating the title compound with an equimolar amount of acetone, is shown in Fig. 1. The structural parameters of **2** revealed that: (i) from the dihedral angles between the least-squares planes, it was found that the plane of the anthracene ring twisted by 55.1° from the plane of the 3-guaiazulenyl group owing to the influence of steric hindrance and repulsion between the hydrogen atoms of the C1 and C8 positions of the 9-anthryl group and the hydrogen atom of the C2′ position of the 3-guaiazulenyl group, which was larger than the dihedral angle observed for that of **3a** (21.3°),[1,2] (ii) similarly, as in the case of **3a**, the 3-guaiazulenylmethylium substituent clearly undergoes bond alternation between the single and double bonds in comparison with the bond distances of the two 3-guaiazulenyl groups of 1,4-bis[(3-guaiazulenyl)methyl]benzene,[1] and (iii) the anthracene ring also clearly undergoes bond alternation between the single and double bonds in comparison with the benzene ring of **3a**.

The electrochemical behavior of **2** was measured by means of CV and DPV (Potential/V vs SCE) in CH_3CN containing 0.1 M [n-Bu_4N]PF_6 as a supporting electrolyte under the same electrochemical conditions as **3a**.[3] From a comparative study with the reduction potentials of **2** and **3a**, it can be inferred that **2** undergoes a one-electron reduction at a potential of -0.26 (E_{pc}, irreversible) V by CV (corresponding to -0.20 (E_p) V by DPV), generating the corresponding 9-anthryl-3-guaiazulenylmethyl radical species, which coincided with that of **3a** [-0.29 (E_{pc}, irreversible) V by CV (corresponding to -0.20 (E_p) V by DPV)].[3]

Similarly, as in the case of **3b**,[2,6] the hydride-reduction of **2** was performed as follows. To a solution of $NaBH_4$ (10 mg, 0.26 mmol) in ethanol (2 mL) was added a solution of **2** (100 mg, 169 µmol) in acetonitrile (1 mL). The mixture was stirred at 25 °C for 20 min and then evaporated in vacuo. The thus-ob-

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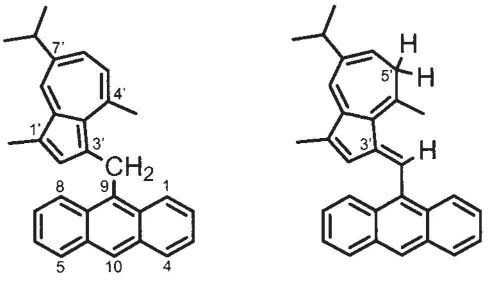

4 **5**

Chart 1. Structural formulas.

tained residue was carefully separated by silica-gel column chromatography with hexane–benzene (4:1, v/v) as an eluant, providing pure compounds **4** (55 mg, 84% yield) and **5** (10 mg, 15% yield). The FAB-MS and ^{1}H NMR (including 2D NMR; namely, H–H COSY and NOESY) studies led to the molecular structures, 9-[(3-guaiazulenyl)methyl]anthracene for **4**,[7] and (*E*)-9-[(5*H*-guaiazulen-3-ylidene)methyl]anthracene for **5**[8] (Chart 1). Although the reduction of **3a** with $NaBH_4$ quantitatively gave (3-guaiazulenylmethyl)benzene,[6] the reduction of **2** with $NaBH_4$ afforded **4** and **5**. This difference can be inferred to arise as follows: The positive charge of **2** is mainly localized at the Cα carbon atom of the 3-guaiazulenylmethylium substituent and, further, slightly transferred to its seven-membered ring, forming the stabilized HC^+-α carbenium- and guaiazulenylium-ions, owing to the influence of larger steric repulsion between the 3-guaiazulenylmethylium substituent and the 9-anthryl group in comparison with the molecular structure of **3a**.

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4 **2**: Dark-blue needles, mp > 100 °C (decomp.); Found: C, 66.63; H, 5.55%, Calcd for $C_{33}H_{33}F_6OP$ (**2**$\cdot$acetone): C, 66.61; H, 5.59%; UV/vis $\lambda_{\max}$ (CH_3CN) nm ($\log \varepsilon$), 213sh (4.52), 254 (5.19), 317 (4.40), 333sh (4.37), 365 (4.12), 387 (4.11), and 588 (3.97); IR $\nu_{\max}$ (KBr) cm^{-1}, 841 and 559 (PF_6^-); exact FAB-MS (matrix: 3-nitrobenzyl alcohol), Found: m/z 387.2142, Calcd for $C_{30}H_{27}$: $[M - PF_6]^+$, 387.2113; ^{1}H NMR (CD_3CN), signals based on the 3-guaiazulenylmethylium substituent: δ 1.48 (6H, d, $J = 6.5$ Hz, $(C\underline{H}_3)_2CH$-7′), 2.25 (3H, d, $J = 1.0$ Hz, Me-1′), 3.53 (1H, sept, $J = 6.5$ Hz, $Me_2C\underline{H}$-7′), 3.54 (3H, s, Me-4′), 7.00 (1H, brd s, H-2′), 8.51 (1H, dd, $J = 11.0$, 2.0 Hz, H-6′), 8.55 (1H, d, $J = 2.0$ Hz, H-8′), 8.67 (1H, d, $J = 11.0$ Hz, H-5′), and 9.46 (1H, s, HC^+-α); signals based on the 9-anthryl group: δ 7.55 (2H, ddd, $J = 8.5$, 7.0, 2.0 Hz, H-3,6), 7.58 (2H, ddd, $J = 8.5$, 7.0, 2.0 Hz, H-2,7), 8.09 (2H, dd, $J = 8.5$, 2.0 Hz, H-4,5), 8.17 (2H, dd, $J = 8.5$, 2.0 Hz, H-1,8), and 8.75 (1H, s, H-10); ^{13}C NMR (CD_3CN), δ 173.5 (C-7′), 163.5 (C-8a′), 158.9 (C-4′), 153.0 (C-3a′), 152.0 (C-5′), 148.2 (HC^+-α), 146.4 (C-1′), 145.7 (C-6′), 145.3 (C-3′), 141.8 (C-2′), 140.2 (C-8′), 132.2 (C-8a,9a), 131.4 (C-9), 131.1 (C-10), 130.2 (C-4a,10a), 130.0 (C-1,8), 128.4 (C-3,6), 126.9 (C-2,7), 126.5 (C-4,5), 40.5 ($Me_2\underline{C}H$-7′), 29.7 (Me-4′), 23.7 ($(\underline{C}H_3)_2CH$-7′), and 13.7 (Me-1′).

5 Crystallographic data for **2**: $C_{33}H_{33}F_6OP$ (FW = 590.59), dark-blue prism (the crystal size, 0.20 × 0.20 × 0.60 mm), orthorhombic, $P2_12_12_1$ (#19), $a = 14.987(3)$ Å, $b = 25.048(7)$ Å, $c = 8.073(4)$ Å, $V = 3030(1)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.294$ g/cm^3, μ (Mo-Kα) = 1.52 cm^{-1}, Scan width = $(0.84 + 0.30 \tan\theta)^\circ$, Scan mode = ω, Scan rate = 8.0°/min, measured reflections = 3958, observed reflections = 3930, No. of parameters = 371, $R1 = 0.068$, $wR2 = 0.199$, Goodness of Fit Indicator = 1.45. 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 203375.

6 The reduction of **3a** with $NaBH_4$ under the same reaction conditions as **3b**[2] also gave as high as 94% yield of (3-guaiazulenylmethyl)benzene.

7 **4**: Blue solid, mp = 214 °C, $R_f = 0.25$ on silica-gel TLC [hexane–benzene (4:1, v/v)]; exact FAB-MS (matrix: 3-nitrobenzyl alcohol), Found: m/z 388.2216, Calcd for $C_{30}H_{28}$: M^+, 388.2191; ^{1}H NMR (C_6D_6), signals based on the 3-guaiazulenylmethyl group: δ 1.20 (6H, d, $J = 7.0$ Hz, $(C\underline{H}_3)_2CH$-7′), 2.04 (3H, s, Me-1′), 2.75 (1H, sept, $J = 7.0$ Hz, $Me_2C\underline{H}$-7′), 3.04 (3H, s, Me-4′), 5.56 (2H, s, CH_2-3′), 6.79 (1H, d, $J = 10.7$ Hz, H-5′), 6.83 (1H, s, H-2′), 7.17 (1H, dd, $J = 10.7$, 2.1 Hz, H-6′), and 8.00 (1H, d, $J = 2.1$ Hz, H-8′); signals based on the 9-anthryl group: δ 7.21 (2H, ddd, $J = 8.8$, 6.5, 1.0 Hz, H-2,7), 7.28 (2H, ddd, $J = 8.3$, 6.5, 1.0 Hz, H-3,6), 7.93 (2H, dd, $J = 8.3$, 1.0 Hz, H-4,5), 8.25 (2H, dd, $J = 8.8$, 1.0 Hz, H-1,8), and 8.31 (1H, s, H-10).

8 **5**: Yellow prisms (from methanol), mp = 147 °C, $R_f = 0.34$ on silica-gel TLC [hexane–benzene (4:1, v/v)]; exact FAB-MS (matrix: 3-nitrobenzyl alcohol), Found: m/z 388.2163, Calcd for $C_{30}H_{28}$: M^+, 388.2191; ^{1}H NMR (C_6D_6), signals based on the 5*H*-guaiazulen-3-ylidene unit: δ 1.10 (6H, d, $J = 7.0$ Hz, $(C\underline{H}_3)_2CH$-7′), 1.64 (3H, d, $J = 1.0$ Hz, Me-1′), 2.35 (3H, s, Me-4′), 2.45 (1H, sept, $J = 7.0$ Hz, $Me_2C\underline{H}$-7′), 2.62 (2H, d, $J = 7.0$ Hz, H-5′), 5.34 (1H, brd dd, $J = 7.0$, 7.0 Hz, H-6′), 5.88 (1H, brd s, H-2′), 6.42 (1H, brd s, H-8′), and 7.23 (1H, brd s, CH-3′); signals based on the 9-anthryl group: δ 7.23 (2H, ddd, $J = 8.6$, 6.6, 1.5 Hz, H-2,7), 7.29 (2H, ddd, $J = 8.3$, 6.6, 1.2 Hz, H-3,6), 7.88 (2H, dd, $J = 8.3$, 1.5 Hz, H-4,5), 8.25 (1H, s, H-10), and 8.31 (2H, dd, $J = 8.6$, 1.2 Hz, H-1,8).