



A facile preparation, the crystal structure, the chemical and electrochemical properties of [4-(dimethylamino)phenyl]-3-guaiazulenylmethylum tetrafluoroborate

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Abstract—Reaction of guaiazulene (**1**) with *p*-dimethylaminobenzaldehyde in methanol in the presence of tetrafluoroboric acid gives the title monocation compound, [4-(dimethylamino)phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**2**), in 90% yield. The title investigations of compound **2** compared with those of two other monocations stabilized by a 3-guaiazulenyl group (i.e. phenyl-3-guaiazulenylmethyl and [4-(isopropyl)phenyl]-3-guaiazulenylmethyl cations) are reported. © 2003 Elsevier Science Ltd. All rights reserved.

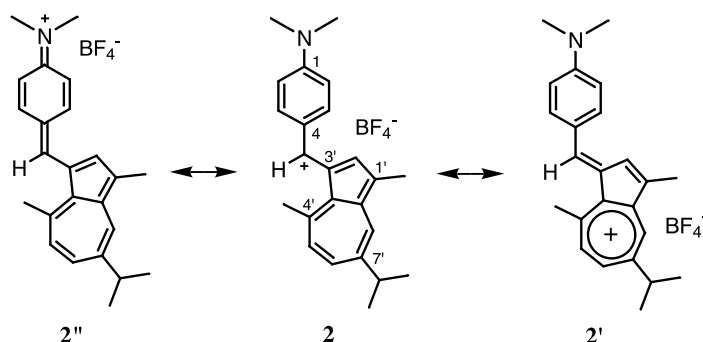
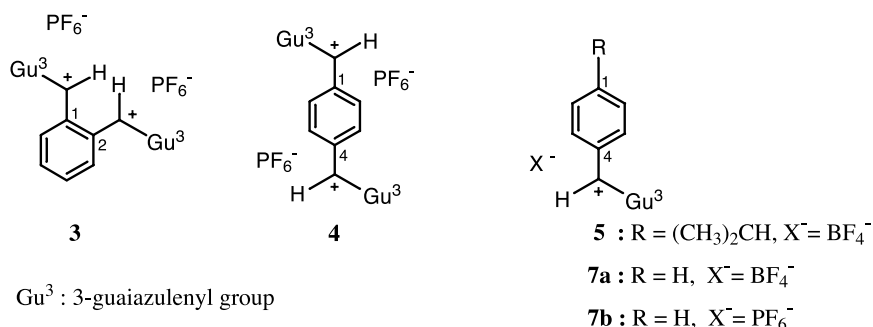
Azulene and its derivatives constitute a highly interesting class of compounds due to the fused 5–7 bicyclic aromatic ring system. These compounds are regarded as one of the representative examples of non-benzenoid aromatic hydrocarbons, which were found to be reluctant to undergo Diels–Alder reactions but easily susceptible to various electrophilic substitution reactions such as acylation, halogenation, nitration, azo-coupling and aminomethylation most easily at the C-1 and/or C-3 position.¹ In particular, naturally occurring guaiazulene (**1**: 1,4-dimethyl-7-isopropylazulene) possesses low oxidation potential ($E^{\text{ox}}+0.65$ V vs SCE)¹ in comparison with those of azulene ($E^{\text{ox}}+0.88$ V vs SCE)¹ and other alkylazulenes ($E^{\text{ox}}+0.88$ – $+0.67$ V vs SCE),¹ and is an interesting compound from the viewpoint of the creation of novel functional materials, with a delocalized π -electron system possessing a 3-guaiazulenyl group (Gu^3), which serves as an electron donor.

As a series of basic studies on the creation of novel functional materials with guaiazulene (**1**), we have been working on a facile preparation, the crystal structures, the spectroscopic and characteristic chemical properties, and further, the electrochemical behavior of carbocations stabilized by a 3-guaiazulenyl group for the past several years, and have reported the investigations of the dicarbocation

compounds, 1,2- and 1,4-phenylenebis(3-guaiazulenylmethylum) bis(hexafluorophosphate)s (**3**^{2,3} and **4**^{2–6}). Furthermore, during the course of our investigations, we recently clarified the crystal structure of a monocation compound, [4-(isopropyl)phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**5**),⁵ which formed a unique π -stacking structure in the single crystal, as the first example for carbocations stabilized by an azulenyl group. Interestingly, the accurate structural parameters of **5** suggested the following two points: (i) although the positive charge of the crystal structure **5** is mainly localized at the C α carbon atom, forming a 3-guaiazulenylmethylum ion, the positive charge apparently is slightly transferred to the seven-membered ring, forming a 3-guaiazulenylum ion; and (ii) formation of a conjugated π -electron system between the 3-guaiazulenylmethylum plane and the isopropylbenzene ring is possible. Now, our interest has been focused on the X-ray crystallographic analysis of the title monocation compound, [4-(dimethylamino)phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**2**), where the formation of the following two representative resonance forms (i.e. 3-guaiazulenylum and quinonoid structures **2'** and **2''**) is possible, and on the properties of this molecule in which a single crystal is formed. [4-(Dimethylamino)phenyl]-3-guaiazulenylmethylum chloride^{7a} and the perchlorate^{7b,c} are known compounds, which were prepared by the reactions of guaiazulene (**1**) with *p*-dimethylaminobenzaldehyde in saturated dry ether with hydrogen chloride and in perchloric acid, respectively; however, nothing has really been documented regarding the accurate spectral data, the crystal structures and the detailed properties of these

Keywords: azulenes; carbonium ions; electrochemistry; electron donors; reduction; X-ray crystal structures.

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compounds. We now wish to report our detailed studies on a facile preparation, the crystal structure, the spectroscopic and characteristic chemical properties, and further, the electrochemical behavior of **2** compared with those of two other monocations stabilized by a 3-guaiazulenyl group (i.e. phenyl-3-guaiazulenylmethyl and [4-(isopropyl)-phenyl]-3-guaiazulenylmethyl cations).

1. Results and discussion

1.1. Preparation and spectroscopic properties of [4-(dimethylamino)phenyl]-3-guaiazulenylmethylium tetrafluoroborate (**2**) and reduction of **2** with NaBH_4

The target compound **2** was prepared in an excellent yield using a methanol as a solvent as shown in Section 3, whose molecular structure was established on the basis of elemental analysis, spectroscopic data [UV–Vis, IR, FAB-MS, ^1H and ^{13}C NMR including 2D NMR (H–H COSY, HMQC= ^1H detected heteronuclear multiple quantum coherence and HMBC= ^1H detected heteronuclear multiple bond connectivity)] and chemical evidence (i.e. the reduction of **2** with NaBH_4).

Compound **2** was a metallic-green block, $\text{mp} > 160^\circ\text{C}$ [decomp., determined by thermal analysis (TGA and DTA)], while a solution of **2** in acetonitrile was dark-blue. The UV–Vis [λ_{max} (CH_3CN) nm] spectrum is shown in Figure 1. A comparative study on the UV–Vis spectra of **2**, 1-dimethylamino-4-(3-guaiazulenylmethyl)benzene (**6**) obtained by the reduction of **2** with NaBH_4 , [4-(isopropyl)-phenyl]-3-guaiazulenylmethylium tetrafluoroborate (**5**)⁵ and phenyl-3-guaiazulenylmethylium tetrafluoroborate (**7a**) showed that: (i) the spectral pattern of the characteristic UV–Vis absorption bands (λ_{max} 200–450 nm) based on the

3-guaiazulenyl group of **2** changed in comparison with that of **6** without a conjugated π -electron system between the 3-guaiazulenyl group and the dimethylaminophenyl group (Fig. 1); and (ii) a characteristic absorption band based on the formation of the [4-(dimethylamino)phenyl]-3-guaiazulenylmethylium moiety with a delocalized π -electron system appeared at the absorption maximum (λ_{max} 638 nm, $\log \epsilon = 4.88$), which showed larger bathochromic shifts and hyperchromic effects in comparison with those of **5** (λ_{max} 472 nm, $\log \epsilon = 4.47$)⁵ and **7a** (λ_{max} 456 nm, $\log \epsilon = 4.24$). Although a solution of **2** in acetonitrile was dark-blue, a solution of **2** in trifluoroacetic acid was yellowish-orange. The UV–Vis [λ_{max} (CF_3COOH) nm] spectral pattern of **2**, whose structure possesses an N–H \cdots O hydrogen bond between the protonated amino group and the trifluoroacetate anion, changed in comparison with that of **2** in acetonitrile, and further, the characteristic near IR absorption bands appeared at λ_{max} 904sh and 1032 nm. The IR (KBr) spectrum showed three specific bands based on the counter anion (BF_4^-) at ν_{max} 1096, 1042 and 521 cm^{-1} , which showed high and low wavenumber-field shifts, respectively, in comparison with those of **5** (ν_{max} 1120sh, 1080, 1049 and 521 cm^{-1})⁵ and **7a** (ν_{max} 1119, 1096, 1084, 1057 and 521 cm^{-1}). The molecular formula $\text{C}_{24}\text{H}_{28}\text{N}$ for the carbocation unit was determined by the exact FAB-MS (3-nitrobenzyl alcohol matrix) spectrum. The elemental analysis confirmed the molecular formula $\text{C}_{24}\text{H}_{28}\text{NBF}_4$. The 500 MHz ^1H NMR (CD_3CN) spectrum showed signals based on the 3-guaiazulenylmethylium substituent with the resonance form of a 3-guaiazulenylmethyl structure and signals based on the dimethylaminophenyl group with the resonance form of a quinonoid structure, whose signals were carefully assigned using the computer-assisted simulation analysis. All the signals of **2** showed larger down-field shifts in comparison with those of **6**, suggesting the formation of the [4-(dimethylamino)phenyl]-

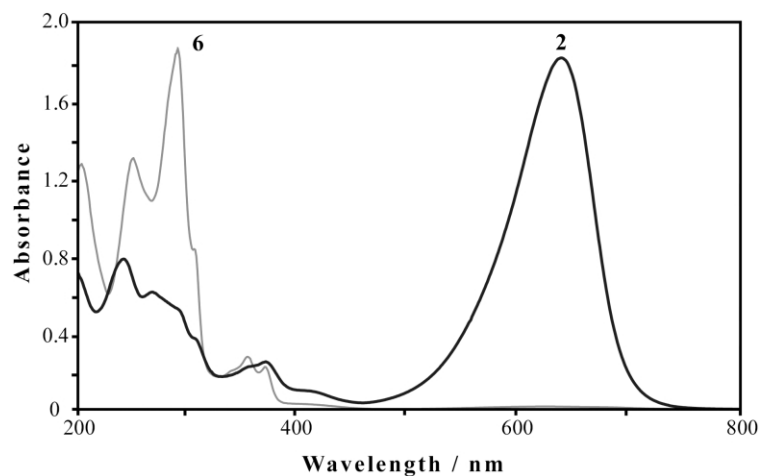


Figure 1. The UV–Vis spectra of compounds **2** and **6** in CH_3CN . Concentrations, **2**: 0.010 g/L (24 $\mu\text{mol/L}$); **6**: 0.146 g/L (441 $\mu\text{mol/L}$). Length of the cells, **2**: 1 cm; **6**: 0.1 cm, respectively.

3-guaiazulenylmethyl cation structure with a delocalized π -electron system for the carbocation unit of **2**. The 125 MHz ^{13}C NMR (CD_3CN) spectrum exhibited twenty carbon signals assigned by HMQC and HMBC techniques. The chemical shifts (δ , ppm) for the proton and carbon signals of the $\text{HC}^+-\alpha$ carbenium-ion center of **2** (8.70 for ^1H NMR; 153.0 for ^{13}C NMR) in acetonitrile- d_3 showed up- and down-field shifts, respectively, in comparison with those of the $\text{HC}^+-\alpha$ carbenium-ion centers of **5** (8.79 for ^1H NMR; 151.0 for ^{13}C NMR) and **7a** (8.80 for ^1H NMR; 150.5 for ^{13}C NMR) in acetonitrile- d_3 . Moreover, the ^1H and ^{13}C NMR spectral data of **2** in trifluoroacetic acid- d_1 , whose structure possesses an $\text{N}-\text{D}\cdots\text{O}$ heavy hydrogen bond between the deuterated amino group and the trifluoroacetate anion, are shown in the Section 3. The chemical shift for the carbon signal of the $\text{HC}^+-\alpha$ carbenium-ion center of **2** (δ 153.0) in trifluoroacetic acid- d_1 coincided with that of the $\text{HC}^+-\alpha$ carbenium-ion center of **2** (δ 153.0) in acetonitrile- d_3 . Along with the above elemental analysis and spectroscopic data of **2**, the reduction of **2** with a 1.5 M amount of NaBH_4 in a

mixed solvent of acetonitrile and ethanol at 25°C for 20 min under aerobic conditions afforded as high as 92% isolated yield of 1-dimethylamino-4-(3-guaiazulenylmethyl)benzene (**6**), in which a hydride ion attached to the $\text{C}\alpha$ position of **2**, selectively. These spectroscopic data compared with those of **5–7a** and the chemical evidence led to the molecular structure, [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl cation tetrafluoroborate with resonance forms of the 3-guaiazulenyl cation and quinonoid structures **2'** and **2''**, for **2** in acetonitrile.

1.2. X-Ray crystal structure of [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl cation tetrafluoroborate (**2**)

The crystal structure of compound **2** was determined by means of X-ray diffraction, producing accurate structural parameters. The ORTEP drawing of **2** compared with that of phenyl-3-guaiazulenylmethyl cation hexafluorophosphate (**7b**), because of difficulty in obtaining single crystals of the tetrafluoroborate **7a** suitable for X-ray crystallographic

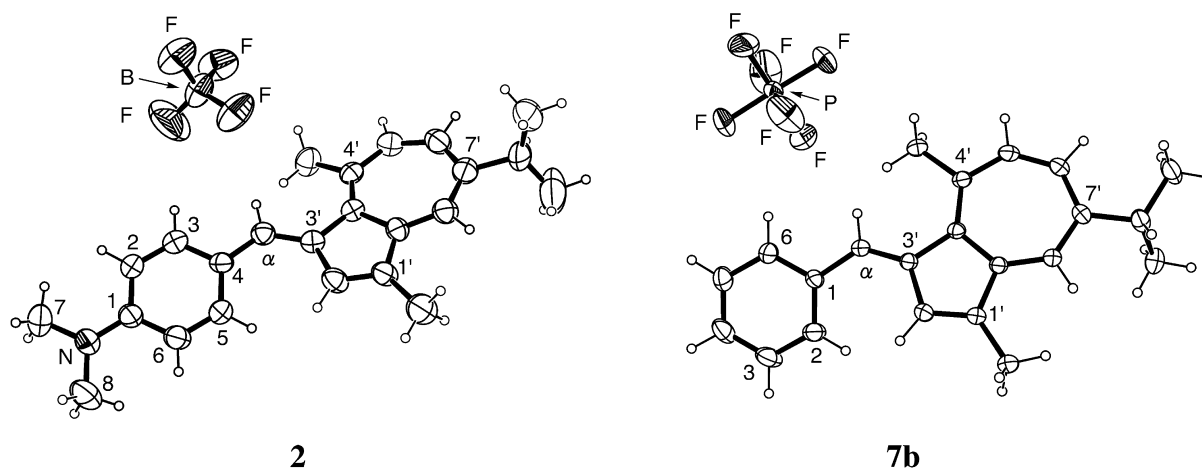


Figure 2. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **2** and **7b**. The selected bond distances (\AA) of **2** are as follows: C1–C2; 1.390(8), C2–C3; 1.372(8), C3–C4; 1.405(7), C4–C5; 1.404(8), C5–C6; 1.360(7), C6–C1; 1.403(8), C1–N; 1.359(7), C4–C α ; 1.414(7), C α –C3'; 1.396(7), C1'–C2'; 1.351(7), C2'–C3'; 1.448(7), C3'–C3a'; 1.457(7), C3a'–C4'; 1.385(7), C4'–C5'; 1.406(7), C5'–C6'; 1.373(8), C6'–C7'; 1.386(8), C7'–C8'; 1.379(8), C8'–C8a'; 1.392(7), C8a'–C1'; 1.416(7) and C8a'–C3a'; 1.465(7). The selected bond distances (\AA) of **7b** are as follows: C1–C2; 1.407(4), C2–C3; 1.376(5), C3–C4; 1.379(5), C4–C5; 1.380(5), C5–C6; 1.384(4), C6–C1; 1.393(4), C1–C α ; 1.461(4), C α –C3'; 1.361(4), C1'–C2'; 1.345(4), C2'–C3'; 1.449(3), C3'–C3a'; 1.481(3), C3a'–C4'; 1.398(3), C4'–C5'; 1.408(4), C5'–C6'; 1.375(4), C6'–C7'; 1.393(4), C7'–C8'; 1.394(4), C8'–C8a'; 1.389(3), C8a'–C1'; 1.459(3) and C8a'–C3a'; 1.450(3).

analysis, is shown in Figure 2 together with the selected bond distances. As the result, 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 dimethylaminobenzene ring twisted by 20.7° from the plane of the 3-guaiazulenyl group owing to the influence of slight steric hindrance between the hydrogen atoms of the C5 and C2' positions, which was smaller than the dihedral angle observed for that of [4-(isopropyl)phenyl]-3-guaiazulenylmethylmethyl tetrafluoroborate (**5**) (40.1°),⁵ and which coincided with that of **7b** (21.3°); (ii) the counter anion (BF_4^-) was located near the C_α carbenium-ion center (the distance between the B– C_α atoms: 4.362 Å), which was shorter than the distance observed for that of **5** (5.647 Å); (iii) similarly, as in the cases of **5** and **7b**, the 3-guaiazulenylmethylmethyl substituent clearly indicated the bond alternation between the single and double bonds in comparison with the bond distances of the parent azulene (**8**)⁸ and 1,4-bis(3-guaiazulenylmethyl)benzene (**9**);⁶ (iv) the average C–C bond distance for the seven-membered ring of the 3-guaiazulenyl group (1.399 Å) coincided with the bond distances observed for those of **5** (1.401 Å) and **7b** (1.401 Å); (v) the bond distances for the five-membered ring of the 3-guaiazulenyl group appreciably varied between 1.352 and 1.466 Å; in particular, the C1'–C2' bond distance (1.352 Å) was characteristically shorter than the average C–C bond distance for the five-membered ring (1.428 Å), which coincided with the bond distances observed for the five-membered rings of **5** and **7b**; (vi) the C_α –C3' bond distance (1.397 Å) was also characteristically shorter than the C4– C_α bond distance (1.415 Å) and although the C_α –C3' bond distance was longer than the bond distances observed for those of **5** (1.364 Å) and **7b** (1.361 Å), the C4– C_α bond distance was shorter than the bond distances observed for those of **5** (1.451 Å) and **7b** (1.461 Å); (vii) the plane of the dimethylamino group was co-planar with that of the benzene ring, and the C1–N bond distance (1.360 Å) coincided with the C–N bond distances (1.368 and 1.371 Å) observed between the nitrogen atoms of the dimethylamino groups and the carbon atoms of the benzene rings for a 1:1 complex of 4,4'-bis(dimethylamino)benzophenone and pentafluorophenol [(*p*-Me₂NPh)₂CO·HOC₆F₅] (**10**)⁹ whose bond distances indicated a small contribution from the following resonance forms in the single crystal (Fig. 3); and (viii) the dimethylaminobenzene ring clearly indicated the bond alternation between the single and double bonds in comparison with the benzene rings of **5** and **7b**, which coincided with a bond alternation pattern observed for the dimethylaminobenzene rings of **10**. Moreover, from a comparative study on the bond distances of **2** with those of **5**, **7b** and **8–10**, it can be inferred that: (i) although the positive charge of **2** in the single crystal is mainly localized at the C_α carbon atom, forming a 3-guaiazulenylmethylmethyl ion, the positive charge apparently is slightly transferred to

the seven-membered ring or the nitrogen atom of the dimethylaminobenzene ring, forming a 3-guaiazulenylmethylmethyl or quinonoid structure **2'** or **2''**; and further, (ii) from the result of the dihedral angle between the least-squares planes of the 3-guaiazulenyl group and the dimethylaminobenzene ring, formation of a conjugated π -electron system between them, which combined with the C_α carbon atom, is possible. Thus, along with the spectroscopic data and the chemical evidence for **2** in acetonitrile, the X-ray crystallographic analysis for **2** also led to the crystal structure, [4-(dimethylamino)phenyl]-3-guaiazulenylmethylmethyl tetrafluoroborate with the resonance forms of the 3-guaiazulenylmethylmethyl and quinonoid structures **2'** and **2''**. Along with the crystal structure of **2**, the packing structure of **2** revealed that this molecule formed a π -stacking structure in the single crystal and that the average inter-plane distance between the over-lapping molecules (i.e. the 3-guaiazulenylmethylmethyl plane of a molecule and the dimethylaminobenzene ring of another molecule), which were overlapped so that those dipole moments might be negated mutually, was 4.20 Å. Thus, the reason why the yield of **2** as single crystals was high (90%) can be inferred to be that **2** readily forms an accumulation (i.e. an inter-molecular π -stacking structure) in the recrystallization solvent, providing the single crystals of **2**, quantitatively.

1.3. A comparative study on the reductions of [4-(dimethylamino)phenyl]-3-guaiazulenylmethylmethyl tetrafluoroborate (**2**) and phenyl-3-guaiazulenylmethylmethyl tetrafluoroborate (**7a**) with zinc powder

Although the reduction of **2** with zinc powder in acetonitrile at 25°C for 1 h under argon gave a number of chromatographically inseparable products, the reduction of **7a** under the same reaction conditions as **2** afforded 1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11**) in 74% isolated yield. The molecular structure **11** was established on the basis of elemental analysis and spectroscopic data [UV–Vis, EI-MS, ^1H and ^{13}C NMR including 2D NMR (H–H COSY, HMQC and HMBC)]. A careful study of the 700 MHz ^1H NMR signals for **11** led us to a ca. 10:9, chromatographically inseparable mixture of *meso* **11a** and two enantiomeric **11b** forms of the molecular structure, 1,2-di(3-guaiazulenyl)-1,2-diphenylethane. An inspection of the molecular models of the most favorable conformations suggested that in the *meso* form **11a** an anisotropic effect exerted by the 3-guaiazulenylphenylmethyl region of the other moiety is likely to cause apparent downfield shifts of the signals for the H-1,2, H-2',2'',6',6'' of the diphenyl groups and Me-1''',1''',4''',4'''' of the di(3-guaiazulenyl) groups in comparison with those of the enantiomers **11b**; moreover, in **11b** the same effect would cause division of the methyl protons of the isopropyl-7''',7'''' into two signals (a ratio of almost 1:1). This enabled us to make the most

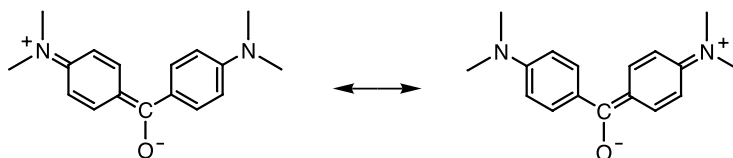


Figure 3. Resonance forms of a 4,4'-bis(dimethylamino)benzophenone moiety for a 1:1 complex of 4,4'-bis(dimethylamino)benzophenone and pentafluorophenol [(*p*-Me₂NPh)₂CO·HOC₆F₅] (**10**)⁹ in the single crystal.

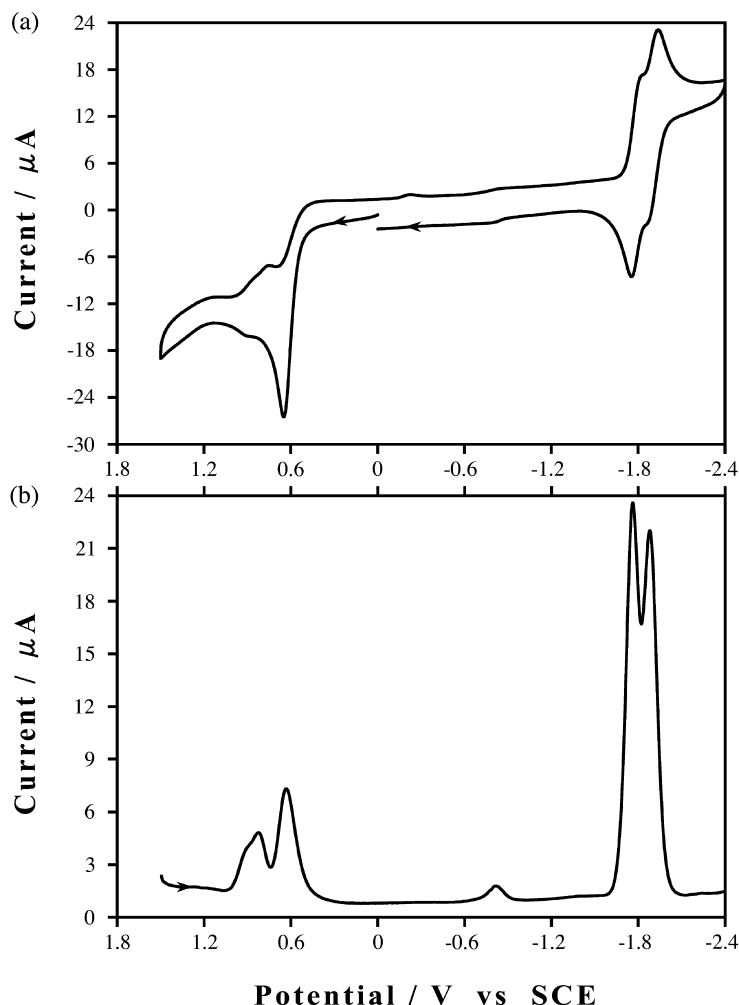
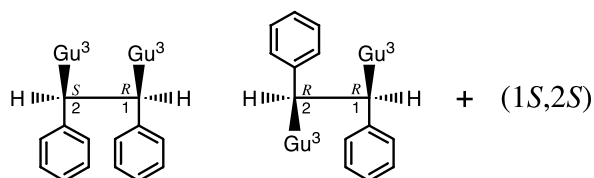


Figure 4. Cyclic (a) and differential pulse (b) voltammograms of compound **11** (3.0 mg, 5.2 μmol) in 0.1 M $[n\text{-Bu}_4\text{N}]\text{BF}_4$, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25°C under argon, respectively. For comparative purposes, the oxidation potential using ferrocene as a standard material showed $+0.45$ (E_p) V by DPV and $+0.42$ ($E_{1/2}$) V by CV under the same electrochemical conditions as **11**.

plausible assignment of all the ^1H NMR signals of these two compounds (see Section 3). Furthermore, the electrochemical behavior of **11** was measured under the same electrochemical conditions as **7a** with a view to a comparative study with those of guaiazulene (**1**)¹⁰ and 3-guaiazulenylmethylbenzene (**12**) obtained by the reduction of **7a** with NaBH_4 . One oxidation and two reduction potentials observed by DPV were positioned at the E_p values of $+0.64$, -1.76 and -1.88 V, while the corresponding one irreversible oxidation and two reversible reduction potentials determined by CV were located at the values of $+0.64$ (E_{pa}), -1.80 ($E_{1/2}$) and -1.92 ($E_{1/2}$) V (Fig. 4). From a comparative study on the redox potentials of **11** with those of **1**¹⁰ and **12**, it can be inferred that: (i) **11** undergoes one-electron oxidation at a potential of $+0.64$ (E_{pa}) V by CV (corresponding to $+0.64$ V by DPV), which coincided with those of **1** [$+0.69$ (E_{pa}) V by CV (corresponding to $+0.65$ V by DPV)] and **12** [$+0.69$ (E_{pa}) V by CV (corresponding to $+0.69$ V by DPV)]; and further, (ii) **11** is stepwise reduced to the di(anion radical) **11**²⁻ at the potentials of -1.80 ($E_{1/2}$) and -1.92 ($E_{1/2}$) V by CV (corresponding to -1.76 and -1.88 V by DPV)]. The value of the one-electron reduction potential (E_1^{red}) of **11** coincided with those of **1** [-1.79 ($E_{1/2}$) V by CV (corresponding to -1.77 V by

DPV)] and **12** [-1.78 ($E_{1/2}$) V by CV (corresponding to -1.76 V by DPV)].



11a (meso)

11b (enantiomers)

Gu^3 : 3-guaiazulenyl group

1.4. Electrochemical behavior of phenyl-3-guaiazulenylmethylm tetrafluoroborate (**7a**) compared with those of [4-(isopropyl)phenyl]-3-guaiazulenylmethylm tetrafluoroborate (**5**) and 1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11**)

We have been interested further in the electrochemical

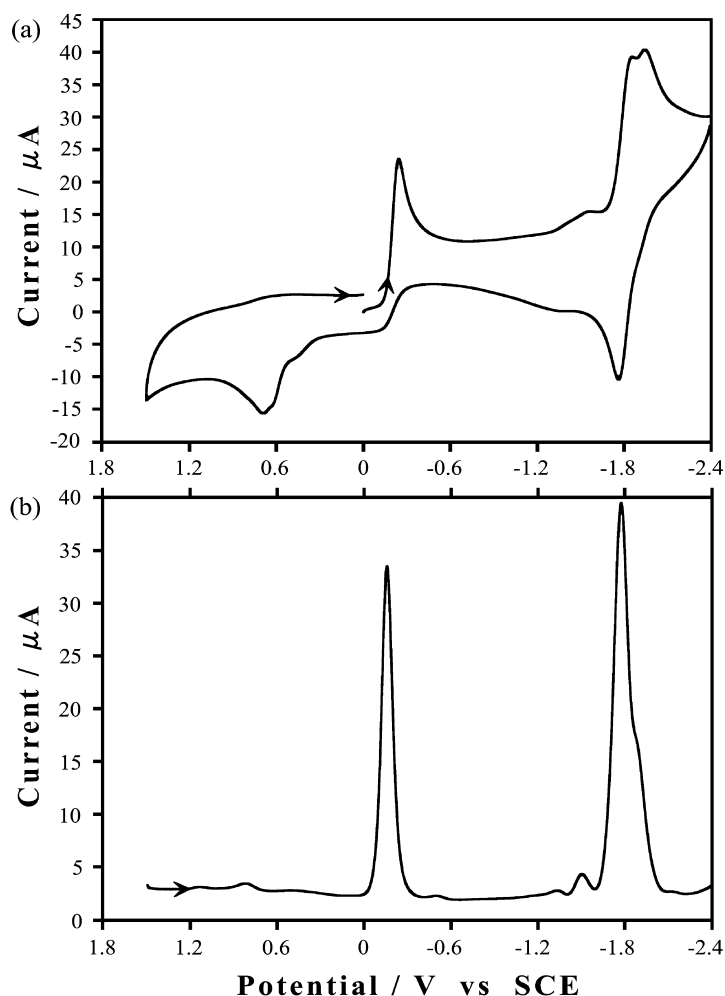


Figure 5. Cyclic (a) and differential pulse (b) voltammograms of compound **7a** (5.0 mg, 13.4 μmol) in 0.1 M $[n\text{-Bu}_4\text{N}]\text{BF}_4$, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25°C under argon, respectively.

properties of the monocarbonium tetrafluoroborate **7a** with a view to a comparative study with those of **2**. The electrochemical behavior of **7a** was, therefore, measured by means of CV and DPV (Potential/V vs SCE) in 0.1 M $[n\text{-Bu}_4\text{N}]\text{BF}_4$, CH_3CN (Fig. 5). Four redox potentials observed by DPV were positioned at the E_p values of -0.16 , -1.50 (a weak wave), -1.78 and -1.89 sh V, while five redox potentials determined by CV were located at the values of $+0.69$ (E_{pa}), -0.25 (E_{pc}), -1.56 (E_{pc} ; a weak wave), -1.81 ($E_{1/2}$) and -1.95 (E_{pc})¹¹ V. From a comparative study on the redox potentials of **7a** with those of [4-(isopropyl)phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**5**) and 1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11**), it can be inferred that: (i) **7a** undergoes one-electron reduction at a potential of -0.25 (E_{pc}) V by CV (corresponding to -0.16 V by DPV), which coincided with that of **5** [-0.27 (E_{pc}) V by CV (corresponding to -0.18 V by DPV)], generating the corresponding 3-guaiazulenylphenylmethyl radical species **a** which is rapidly converted into the radical homo-coupling product **11**; furthermore, (ii) a small amount of the existing radical species **a** without the radical homo-coupling is reduced to the corresponding 3-guaiazulenylphenylmethyl anion species **b** at a potential of -1.56 (E_{pc}) V by CV (corresponding to -1.50 V by DPV), which coincided with that of **5** [-1.56 (E_{pc}) V by CV (corresponding to

-1.50 V by DPV)]. These reduction potentials were the same values as the two-electron reduction potentials (E_2^{red}) of several azulenylmethyl cations, giving the corresponding azulenylmethyl anions, reported by Asao and his co-workers;¹² (iii) the dimer **11** yielded on the surface of the working electrode is stepwise reduced to the di(anion radical) **11**²⁻ at the potentials of -1.81 ($E_{1/2}$) and -1.95 (E_{pc})¹¹ V by CV (corresponding to -1.78 and -1.89 sh V by DPV), whose stepwise reduction potentials were established by those of **11** [-1.80 ($E_{1/2}$) and -1.92 ($E_{1/2}$) V by CV (corresponding to -1.76 and -1.88 V by DPV)] isolated from the reduction of **7a** with zinc powder; and further, (iv) the dimer **11** yielded undergoes two-electron oxidation at a potential of $+0.69$ (E_{pa}) V, which coincided with that of the isolated **11** [$+0.64$ (E_{pa}) V by CV (corresponding to $+0.64$ V by DPV)].

1.5. Electrochemical behavior of [4-(dimethylamino)-phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**2**) compared with those of [4-(isopropyl)phenyl]-3-guaiazulenylmethylum tetrafluoroborate (**5**) and phenyl-3-guaiazulenylmethylum tetrafluoroborate (**7a**)

Similarly, as in the case of **7a**, the electrochemical behavior of **2** was measured by means of CV and DPV (Potential/V vs SCE) in 0.1 M $[n\text{-Bu}_4\text{N}]\text{BF}_4$, CH_3CN (Fig. 6). Five

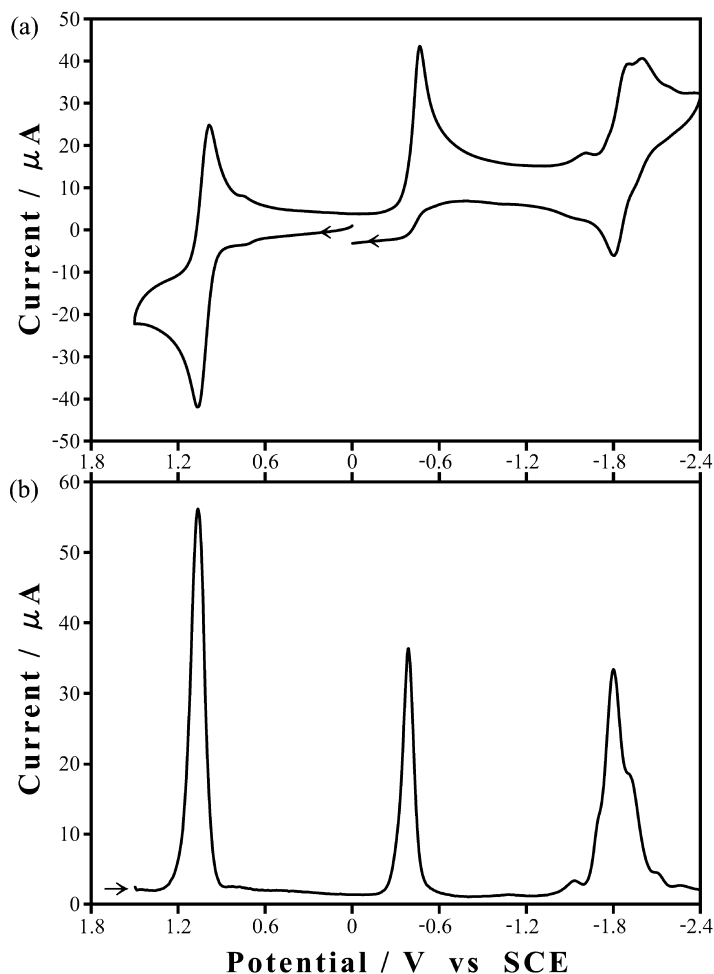


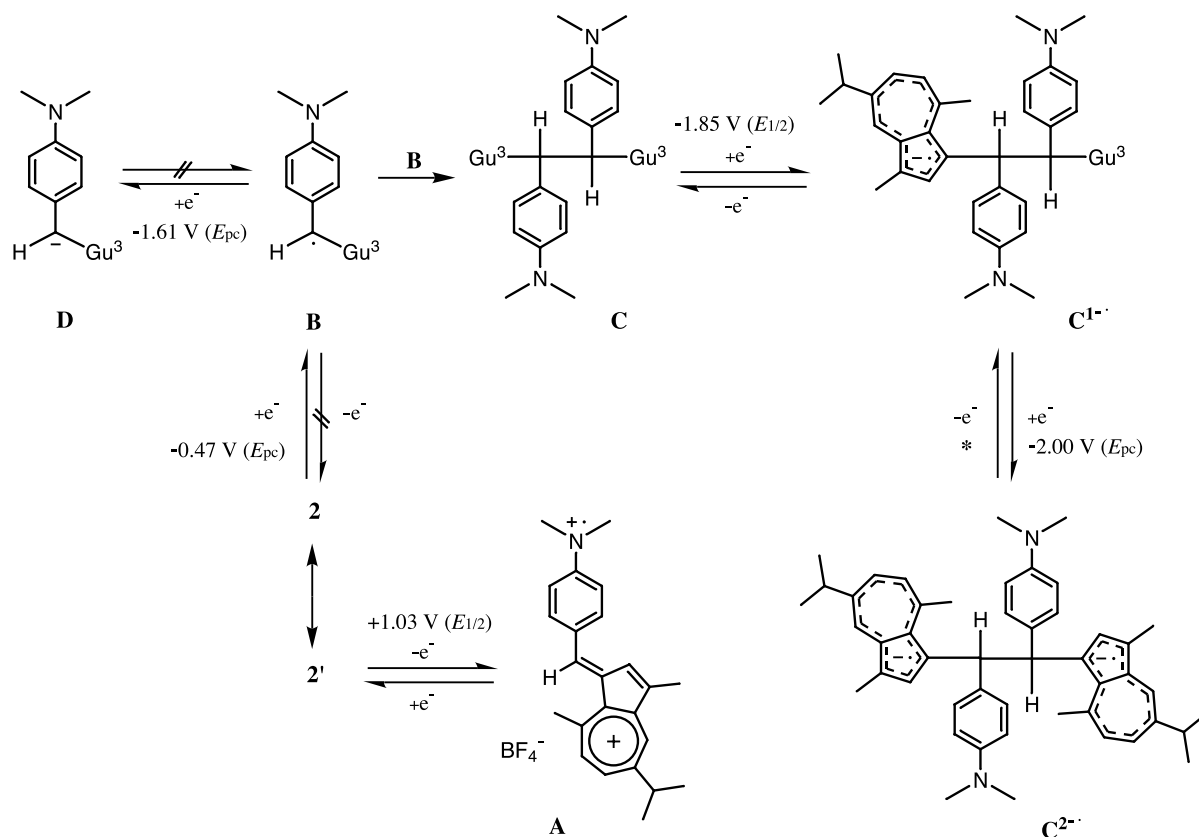
Figure 6. Cyclic (a) and differential pulse (b) voltammograms of compound **2** (6.0 mg, 14.4 μmol) in 0.1 M $[n\text{-Bu}_4\text{N}]\text{BF}_4$, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25°C under argon, respectively.

redox potentials observed by DPV were positioned at the E_p values of +1.06, -0.39 , -1.54 (a weak wave), -1.80 and -1.92sh V , while the corresponding five redox potentials determined by CV were located at the values of +1.03 ($E_{1/2}$), -0.47 (E_{pc}), -1.61 (E_{pc} ; a weak wave), -1.85 ($E_{1/2}$) and -2.00 (E_{pc})¹¹ V. From a comparative study on the redox potentials of **2** with those of [4-(isopropyl)phenyl]-3-guaiazulenylmethyl tetrafluoroborate (**5**), 1-dimethylamino-4-(3-guaiazulenylmethyl)benzene (**6**) and phenyl-3-guaiazulenylmethyl tetrafluoroborate (**7a**), it can be inferred that: (i) **2** undergoes one-electron oxidation at a potential of +1.03 ($E_{1/2}$) V by CV (corresponding to +1.06 V by DPV), generating an electrochemically stable dication radical **A**, in comparison with that of **6**, via the resonance form of the 3-guaiazulenyl cation structure **2'**; and further, (ii) **2** undergoes one-electron reduction at a potential of -0.47 (E_{pc}) V by CV (corresponding to -0.39 V by DPV), which indicates **2** is less susceptible to reduction in comparison with those of **5** [-0.27 (E_{pc}) V by CV (corresponding to -0.18 V by DPV)] and **7a** [-0.25 (E_{pc}) V by CV (corresponding to -0.16 V by DPV)], generating the corresponding 3-(4-1-dimethylamino-phenyl)guaiazulenylmethyl radical species **B**. The **B** generated is rapidly converted into the radical homocoupling product **C**; furthermore, (iii) a small amount of the existing radical species **B** without the radical homo-

coupling is reduced to the corresponding 3-(4-1-dimethylaminophenyl)guaiazulenylmethyl anion species **D** at a potential of -1.61 (E_{pc}) V by CV (corresponding to -1.54 V by DPV), which coincided with those of **5** and **7a** [-1.56 (E_{pc}) V by CV (corresponding to -1.50 V by DPV), respectively]; and (iv) the dimer **C** yielded on the surface of the working electrode is stepwise reduced to the di(anion radical) C^{2-} at the potentials of -1.85 ($E_{1/2}$) and -2.00 (E_{pc})¹¹ V by CV (corresponding to -1.80 and -1.92sh V by DPV), whose stepwise reduction potentials are supported by those of **11** [-1.80 ($E_{1/2}$) and -1.92 ($E_{1/2}$) V by CV (corresponding to -1.76 and -1.88 V by DPV)] isolated from the reduction of **7a** with zinc powder. From a comparative study on the redox potentials of **2** with those of **1**,¹⁰ **5**, **6**, **7a**, **11** and **12**, a plausible electron transfer mechanism of **2** based on its CV and DPV data is illustrated in Scheme 1. Thus, the CV datum indicated **2** serves as an electron donor.

2. Conclusion

We have reported the following six points in this paper: (i) the reaction of guaiazulene (**1**) with an equimolar amount of *p*-dimethylaminobenzaldehyde in methanol in the presence of tetrafluoroboric acid at 25°C for 2 h under aerobic



Scheme 1. A plausible electron transfer mechanism based on the CV and DPV data of **2**. *The potential of the E_{pa} (V) is included in the half-wave potential of -1.85 ($E_{1/2}$) V.

conditions gave the title monocation compound **2**, quantitatively; (ii) the recrystallization of **2** from acetonitrile–diethyl ether (1:4, v/v) (several times) provided pure **2** as stable single crystals suitable for X-ray crystallographic analysis in 90% isolated yield; (iii) the spectroscopic data for **2** compared with those of **5**, **6** and **7a** and the chemical evidence (i.e. the reduction of **2** with NaBH_4) led to the molecular structure, [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl cation tetrafluoroborate with resonance forms of the 3-guaiazulenylmethyl cation and quinonoid structures **2'** and **2''** in acetonitrile; (iv) along with the spectroscopic data and the chemical evidence for **2** in acetonitrile, the X-ray crystallographic analysis for **2** compared with those of **5** and **7b** also led to the crystal structure, [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl cation tetrafluoroborate with resonance forms of the 3-guaiazulenylmethyl cation and quinonoid structures **2'** and **2''**; (v) although the reduction of **2** with zinc powder in acetonitrile at 25°C for 1 h under argon gave a number of chromatographically inseparable products, the reduction of **7a** under the same reaction conditions as **2** afforded 1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11**), which was a ca. 10:9, chromatographically inseparable mixture of *meso* **11a** and two enantiomeric **11b** forms, in 74% isolated yield; and (vi) the CV datum indicated **2** serves as an electron donor; moreover, a comparative study on the redox potentials of **2** with those of **1**, **5**, **6**, **7a**, **11** and **12** enabled us to submit a plausible electron transfer mechanism of **2** based on its CV and DPV data as shown in Scheme 1.

3. Experimental

3.1. General

Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder, respectively. MS 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 ^1H and 125 MHz for ^{13}C) and JNM-ECA700 (700 MHz for ^1H and 176 MHz for ^{13}C) cryospectrometers at 25°C. The ^1H NMR spectra were assigned using the computer-assisted simulation analysis (the software: gNMR developed by Adept Scientific plc) on a DELL Dimension XPS T500 personal-computer with a Pentium III processor. Cyclic and differential pulse voltammograms were measured by an ALS Model 600 electrochemical analyzer.

3.1.1. Preparation of [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl cation tetrafluoroborate (2**).** To a solution of guaiazulene (**1**) (40 mg, 0.20 mmol) in methanol (1 mL) was added a solution of *p*-dimethylaminobenzaldehyde (30 mg, 0.20 mmol) in methanol (2 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.12 mL). The mixture was stirred at 25°C for 2 h under aerobic conditions, giving a precipitation of a dark-green solid of **2**, and then

was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:4, v/v) (several times) to provide pure **2** as stable single crystals (75 mg, 90% yield).

2: Metallic-green blocks, mp > 160°C [decomp., determined by thermal analysis (TGA and DTA)]; Found: C, 69.60; H, 6.68; N, 3.18%. Calcd for C₂₄H₂₈NBF₄: C, 69.08; H, 6.76; N, 3.36%; UV–Vis λ_{max} (CH₃CN) nm (log ε), 241 (4.51), 267 (4.40), 293sh (4.32), 307sh (4.18), 353sh (3.96), 370 (4.01), 417sh (3.56) and 638 (4.88); UV–Vis λ_{max} (CF₃COOH) nm (log ε), 275 (4.29), 326sh (4.19), 358 (4.41), 441 (4.27), 511 (3.87), 904sh (2.38) and 1032 (2.52); IR ν_{max} (KBr) cm⁻¹, 1096, 1042 and 521 (BF₄⁻); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: *m/z* 330.2208; calcd for C₂₄H₂₈N: [M–BF₄]⁺, *m/z* 330.2222; 500 MHz ¹H NMR (CD₃CN), signals based on the 3-guaiazulenylmethyl group: δ 1.43 (6H, d, *J*=7.0 Hz, (CH₃)₂CH-7'), 2.59 (3H, d, *J*=1.0 Hz, Me-1'), 3.27 (3H, s, Me-4'), 3.37 (1H, sept, *J*=7.0 Hz, Me₂CH-7'), 8.07 (1H, d, *J*=11.0 Hz, H-5'), 8.11 (1H, dd, *J*=11.0, 2.0 Hz, H-6'), 8.18 (1H, brd s, H-2'), 8.49 (1H, d, *J*=2.0 Hz, H-8') and 8.70 (1H, brd s, HC⁺-α); signals based on the dimethylaminophenyl group: δ 3.26 (6H, s, (CH₃)₂N-1), 6.97 (2H, ddd, *J*=8.0, 3.0, 1.0 Hz, H-2,6) and 7.94 (2H, brd ddd, *J*=8.0, 3.0, 1.0 Hz, H-3,5); 125 MHz ¹³C NMR (CD₃CN), δ 161.4 (C-7'), 156.8 (C-1), 154.3 (C-4'), 153.8 (C-8a'), 153.0 (HC⁺-α), 149.8 (C-3a'), 143.6 (C-5'), 142.14 (C-6'), 142.06 (C-2'), 140.0 (C-3,5), 139.5 (C-1'), 138.5 (C-8'), 131.8 (C-3'), 124.9 (C-4), 115.0 (C-2,6), 41.1 (Me₂N-1), 39.5 (Me₂CH-7'), 30.1 (Me-4'), 24.2 ((CH₃)₂CH-7') and 13.5 (Me-1'); 500 MHz ¹H NMR (CF₃COOD), signals based on the 3-guaiazulenylmethyl group: δ 1.53 (6H, d, *J*=7.0 Hz, (CH₃)₂CH-7'), 2.53 (3H, brd s, Me-1'), 3.42 (3H, brd s, Me-4'), 3.47 (1H, sept, *J*=7.0 Hz, Me₂CH-7'), 7.81 (1H, brd s, C-2'), 8.45 (1H, brd dd, *J*=11.0, 2.0 Hz, H-6'), 8.60 (1H, brd d, *J*=11.0 Hz, H-5'), 8.66 (1H, brd d, *J*=2.0 Hz, H-8') and 8.74 (1H, brd s, HC⁺-α); signals based on the deuterated dimethylaminophenyl group: δ 3.51 (6H, s, (CH₃)₂DN⁺-1), 7.84 (2H, brd d, *J*=8.5 Hz, H-2,6) and 7.94 (2H, brd d, *J*=8.5 Hz, H-3,5); 125 MHz ¹³C NMR (CF₃COOD), δ 176.8 (C-7'), 165.1 (C-1), 159.9 (C-8a'), 155.5 (C-4'), 153.0 (HC⁺-α), 149.4 (C-3a'), 147.6 (C-5'), 146.8 (C-6'), 145.8 (C-1'), 144.4 (C-3'), 141.9 (C-2'), 140.58 (C-8'), 140.55 (C-4), 136.2 (C-3,5), 123.4 (C-2,6), 49.7 (Me₂DN⁺-1), 42.6 (Me₂CH-7'), 30.2 (Me-4'), 24.6 ((CH₃)₂CH-7') and 14.3 (Me-1'); DPV (*E*_p), +1.06, -0.39, -1.54 (a weak wave), -1.80 and -1.92sh V; CV, +1.03 (*E*_{1/2}), -0.47 (*E*_{pc}), -1.61 (*E*_{pc}; a weak wave), -1.85 (*E*_{1/2}) and -2.00 (*E*_{pc}) V under the electrochemical conditions shown in the Figure 6.

3.1.2. Reduction of [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl tetrafluoroborate (2) with NaBH₄. To a solution of NaBH₄ (4 mg, 106 μmol) in ethanol (1 mL) was added a solution of **2** (30 mg, 72 μmol) in acetonitrile (2 mL). The mixture was stirred at 25°C for 20 min under aerobic conditions and then evaporated in vacuo. The residue thus obtained was dissolved in hexane and filtered. The hexane filtrate was evaporated in vacuo, giving pure 1-dimethylamino-4-(3-guaiazulenylmethyl)benzene (**6**) as a greenish-blue paste (22 mg, 92% yield).

6: *R*_f=0.64 on silica-gel TLC (hexane–AcOEt–Et₂NH=85:15:0.3, v/v/v); UV–Vis λ_{max} (CH₃CN) nm (log ε), 203 (4.46), 250 (4.47), 290 (4.63), 305 (4.27), 353 (3.79), 369 (3.70), 406sh (2.80), 624 (2.53), 680sh (2.41) and 750sh (1.61); EI-MS (70 eV), *m/z* 331 (M⁺, 100%), 316 ([M–Me]⁺, 55), 288 ([M–*i*-Pr]⁺, 16), 198 (1⁺, 18), 183 ([1–Me]⁺, 19) and 134 ([M–Gu³]⁺, 28); exact EI-MS (70 eV), found: *m/z* 331.2319; calcd for C₂₄H₂₉N: M⁺, *m/z* 331.2300; 500 MHz ¹H NMR (CD₃CN), signals based on the 3-guaiazulenylmethyl group: δ 1.32 (6H, d, *J*=7.0 Hz, (CH₃)₂CH-7'), 2.58 (3H, s, Me-1'), 2.82 (3H, s, Me-4'), 3.03 (1H, sept, *J*=7.0 Hz, Me₂CH-7'), 4.46 (2H, s, CH₂-3'), 6.80 (1H, d, *J*=11.0 Hz, H-5'), 7.29 (1H, dd, *J*=11.0, 2.0 Hz, H-6'), 7.39 (1H, s, H-2') and 8.11 (1H, d, *J*=2.0 Hz, H-8'); signals based on the dimethylaminophenyl group: δ 2.83 (6H, s, (CH₃)₂N-1), 6.65 (2H, ddd, *J*=8.0, 3.0, 1.0 Hz, H-2,6) and 6.83 (2H, brd ddd, *J*=8.0, 3.0, 1.0 Hz, H-3,5); DPV (*E*_p), +1.08, +0.87, +0.72 and -1.80 V; CV, +1.06 (*E*_{pa}), +0.83 (*E*_{pa}), +0.63 (*E*_{pa}) and -1.83 (*E*_{1/2}) V under the same electrochemical conditions as **2**.

3.1.3. X-Ray crystal structure of [4-(dimethylamino)phenyl]-3-guaiazulenylmethyl tetrafluoroborate (2).

A total 4008 reflections with 2θ_{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. Hydrogen atoms were included but not refined. 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 190065.

Crystallographic data for **2**: C₂₄H₂₈NBF₄ (FW=417.30), metallic-green block (the crystal size, 0.30×0.20×0.30 mm), monoclinic, *P*2₁/*n* (#14), *a*=10.563(3) Å, *b*=16.435(3) Å, *c*=13.935(3) Å, β=111.27(2)°, *V*=2254.4(9) Å³, *Z*=4, *D*_{calcd}=1.229 g/cm³, μ(Mo Kα)=0.93 cm⁻¹, Scan width=(1.15+0.30 tan θ)°, Scan mode=ω-2θ, Scan rate=8.0°/min, measured reflections=4008, observed reflections=2805, No. of parameters=271, *R*₁=0.081, *wR*₂=0.232 and Goodness of Fit Indicator=1.76.

3.1.4. Preparation of [4-(isopropyl)phenyl]-3-guaiazulenylmethyl tetrafluoroborate (5). To a solution of guaiazulene (**1**) (50 mg, 0.25 mmol) in acetic acid (0.4 mL) was added a solution of 4-isopropylbenzaldehyde (80 μL, 0.53 mmol) in acetic acid (0.3 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.18 mL). The mixture was stirred at 25°C for 2 h under aerobic conditions. After the reaction, diethyl ether (3.0 mL) was slowly added and the mixture was allowed to stand at 25°C for 24 h, affording single crystals of **5**. The crystals thus obtained were carefully washed with diethyl ether and dried well in a vacuum desiccator to provide pure **5** as stable single crystals (60 mg, 58% yield).

5: Reddish-orange needles, mp 160.8°C [determined by thermal analysis (TGA and DTA)]; Found: C, 72.09; H, 6.89%. Calcd for C₂₅H₂₉BF₄: C, 72.13; H, 7.02%; UV–Vis λ_{\max} (CH₃CN) nm (log ϵ), 226 (4.41), 250sh (4.25), 295 (4.16), 326 (4.08), 392 (4.21) and 472 (4.47); IR ν_{\max} (KBr) cm⁻¹, 1120sh, 1080, 1049 and 521 (BF₄⁻); 500 MHz ¹H NMR (CD₃CN), signals based on the 3-guaiazulenylmethylmethyl substituent: δ 1.47 (6H, d, $J=7.0$ Hz, (CH₃)₂CH-7'), 2.54 (3H, d, $J=1.0$ Hz, Me-1'), 3.38 (3H, s, Me-4'), 3.51 (1H, sept, $J=7.0$ Hz, Me₂CH-7'), 8.06 (1H, brd s, H-2'), 8.44 (1H, dd, $J=11.0, 2.0$ Hz, H-6'), 8.53 (1H, d, $J=11.0$ Hz, H-5'), 8.61 (1H, d, $J=2.0$ Hz, H-8') and 8.79 (1H, brd s, HC⁺- α); signals based on the isopropylphenyl group: δ 1.32 (6H, d, $J=7.0$ Hz, (CH₃)₂CH-1), 3.06 (1H, sept, $J=7.0$ Hz, Me₂CH-1), 7.53 (2H, ddd, $J=8.0, 1.5, 1.0$ Hz, H-2,6) and 7.82 (2H, brd ddd, $J=8.0, 1.5, 1.0$ Hz, H-3,5); 125 MHz ¹³C NMR (CD₃CN), δ 171.4 (C-7'), 161.2 (C-8a'), 157.9 (C-4'), 155.6 (C-3a'), 153.9 (C-1'), 151.0 (HC⁺- α), 150.5 (C-5'), 145.9 (C-3'), 145.0 (C-6'), 141.7 (C-2'), 139.9 (C-8'), 139.7 (C-4), 134.4 (C-3,5), 134.3 (C-1), 128.8 (C-2,6), 40.3 (Me₂CH-7'), 35.1 (Me₂CH-1), 29.9 (Me-4'), 23.9 ((CH₃)₂CH-7'), 23.8 ((CH₃)₂CH-1) and 13.9 (Me-1'); DPV (E_p), -0.18, -1.50 and -1.76 V; CV, +0.75 (E_{pa}), -0.27 (E_{pc}), -1.56 (E_{pc}) and -1.80 ($E_{1/2}$) V under the same electrochemical conditions as **2**.

3.1.5. Preparation of phenyl-3-guaiazulenylmethylmethyl tetrafluoroborate (7a). To a solution of guaiazulene (**1**) (100 mg, 0.50 mmol) in acetic acid (0.5 mL) was added a solution of benzaldehyde (80 μ L, 0.77 mmol) in acetic acid (0.5 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.3 mL). The mixture was stirred at 25°C for 1.5 h under aerobic conditions, giving a precipitation of a reddish-orange solid of **7a**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:4, v/v) (several times) to provide pure **7a** as stable single crystals (133 mg, 71% yield).

7a: Reddish-orange blocks, mp >160°C [decomp., determined by thermal analysis (TGA and DTA)]; Found: C, 70.38; H, 6.15%. Calcd for C₂₂H₂₃BF₄: C, 70.61; H, 6.20%; UV–Vis λ_{\max} (CH₃CN) nm (log ϵ), 204 (4.36), 218 (4.39), 242 (4.37), 292 (4.37), 307sh (4.19), 327 (4.01), 374 (4.19), 390sh (4.14) and 456 (4.24); IR ν_{\max} (KBr) cm⁻¹, 1119, 1096, 1084, 1057 and 521 (BF₄⁻); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 287.1820; calcd for C₂₂H₂₃: [M–BF₄]⁺, m/z 287.1800; 500 MHz ¹H NMR (CD₃CN), signals based on the 3-guaiazulenylmethylmethyl substituent: δ 1.48 (6H, d, $J=7.0$ Hz, (CH₃)₂CH-7'), 2.53 (3H, d, $J=1.0$ Hz, Me-1'), 3.38 (3H, s, Me-4'), 3.52 (1H, sept, $J=7.0$ Hz, Me₂CH-7'), 8.00 (1H, brd s, H-2'), 8.46 (1H, dd, $J=11.0, 2.0$ Hz, H-6'), 8.57 (1H, d, $J=11.0$ Hz, H-5'), 8.61 (1H, d, $J=2.0$ Hz, H-8') and 8.80 (1H, brd s, HC⁺- α); signals based on the phenyl group: δ 7.620 (2H, ddd, $J=8.0, 7.5, 1.5$ Hz, H-3,5), 7.624 (1H, dddd, $J=7.5, 7.5, 1.0, 1.0$ Hz, H-4) and 7.83 (2H, ddd, $J=8.0, 1.5, 1.0$ Hz, H-2,6); 125 MHz ¹³C NMR (CD₃CN), δ 172.1 (C-7'), 161.7 (C-8a'), 158.2 (C-4'), 153.8 (C-3a'), 151.0 (C-5'), 150.5 (HC⁺- α), 146.4 (C-1'), 145.2 (C-6'), 141.5 (C-2'), 140.5 (C-3'), 140.0 (C-8'), 136.6 (C-1), 133.7 (C-2,6), 133.0 (C-4), 130.4 (C-3,5), 40.3 (Me₂CH-7'), 29.8 (Me-4'), 23.8

((CH₃)₂CH-7') and 13.8 (Me-1'); DPV (E_p), -0.16, -1.50 (a weak wave), -1.78 and -1.89sh V; CV, +0.62sh (E_{pa}), +0.69 (E_{pa}), -0.25 (E_{pc}), -1.56 (E_{pc} : a weak wave), -1.81 ($E_{1/2}$) and -1.95 (E_{pc}) V under the same electrochemical conditions as **2**.

3.1.6. Preparation of phenyl-3-guaiazulenylmethylmethyl hexafluorophosphate (7b). To a solution of guaiazulene (**1**) (100 mg, 0.50 mmol) in methanol (1.5 mL) was added a solution of benzaldehyde (80 μ L, 0.77 mmol) in methanol (0.5 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25°C for 1.5 h under aerobic conditions, giving a precipitation of a reddish-orange solid of **7b**, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:4, v/v) (several times) to provide pure **7b** as stable single crystals (208 mg, 96% yield) suitable for X-ray crystallographic analysis.

7b: Reddish-orange blocks, mp >147°C [decomp., determined by thermal analysis (TGA and DTA)]; Found: C, 60.97; H, 5.15%. Calcd for C₂₂H₂₃F₆P: C, 61.11; H, 5.36%; UV–Vis λ_{\max} (CH₃CN) nm (log ϵ), 220 (4.36), 244sh (4.29), 287 (4.20), 326 (4.03), 380 (4.26) and 456 (4.30); IR ν_{\max} (KBr) cm⁻¹, 837 and 556 (PF₆⁻); FAB-MS (3-nitrobenzyl alcohol matrix), m/z 287 [M–PF₆]⁺; All the signals of the ¹H and ¹³C NMR spectra of **7b** in acetonitrile-d₃ coincided with those of **7a**.

3.1.7. X-Ray crystal structure of phenyl-3-guaiazulenylmethylmethyl hexafluorophosphate (7b). A total 4869 reflections with $2\theta_{\max}=55.1^\circ$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda=0.71069$ 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. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2 . All calculations were performed using the teXsan crystallographic software package. The deposition number CCDC: 192216.

Crystallographic data for **7b**: C₂₂H₂₃F₆P (FW=432.39), reddish-orange block (the crystal size, 0.60×0.60×0.50 mm), triclinic, $P-1$ (#2), $a=10.217(1)$ Å, $b=13.980(2)$ Å, $c=7.865(1)$ Å, $\alpha=93.56(1)^\circ$, $\beta=110.422(10)^\circ$, $\gamma=72.22(1)^\circ$, $V=1001.3(2)$ Å³, $Z=2$, $D_{\text{calcd}}=1.434$ g/cm³, $\mu(\text{Mo K}\alpha)=1.97$ cm⁻¹, Scan width=($1.31+0.30 \tan \theta$)°, Scan mode= $\omega-2\theta$, Scan rate=16.0°/min, measured reflections=4869, observed reflections=4607, No. of parameters=262, $R1=0.071$, $wR2=0.243$ and Goodness of Fit Indicator=2.21.

3.1.8. Reduction of phenyl-3-guaiazulenylmethylmethyl tetrafluoroborate (7a) with zinc powder. To a solution of **7a** (50 mg, 134 μ mol) in acetonitrile (1.5 mL) was added a zinc powder (100 mg, 1.53 mmol) under argon. The mixture was stirred at 25°C for 1 h under argon. After the reaction, the zinc powder was removed by using a centrifugal separator. The reaction solution was evaporated in vacuo, giving a blue paste residue, which was carefully

separated by silica-gel column chromatography with hexane–ethyl acetate (4:1, v/v) as an eluant. The crude product, 1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11**), thus obtained was recrystallized from methanol (several times) to provide a ca. 10:9, chromatographically inseparable mixture of *meso*, (1*R*,2*S*)-1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11a**) and two enantiomeric, (1*R*,2*R*)- and (1*S*,2*S*)-1,2-di(3-guaiazulenyl)-1,2-diphenylethane (**11b**), forms as stable crystals (28 mg, 73% yield).

11: $R_f=0.59$ on silica-gel TLC (AcOEt–hexane=1:4, v/v); blue prisms, mp>220°C [decomp., determined by thermal analysis (TGA and DTA)]; Found: C, 90.60; H, 8.10%. Calcd for $C_{88}H_{94}O$ [$2(C_{44}H_{46})\cdot H_2O$]: C, 90.52; H, 8.11%; UV–Vis λ_{max} (CH_2Cl_2) nm (log ϵ), 218 (4.53), 249 (4.64), 297 (4.84), 310 (4.68), 358 (4.17), 374 (4.23), 624 (2.91), 683sh (2.79) and 763sh (2.09); EI-MS (70 eV), m/z 574 (M^+ , 0.86%) and 286 ($[1/2M-H]^+$, 100); exact EI-MS (70 eV), found: m/z 574.3595; calcd for $C_{44}H_{46}$: M^+ , m/z 574.3600; DPV (E_p), +0.64, –1.76 and –1.88 V; CV, +0.64 (E_{pa}), –1.80 ($E_{1/2}$) and –1.92 ($E_{1/2}$) V under the same electrochemical conditions as **2**. The relative intensity of the 1H NMR signals for the *meso* **11a** and the enantiomers **11b** showed a ratio of ca. 10:9.

11a: 700 MHz 1H NMR (CD_2Cl_2), signals based on the 1,2-di(3-guaiazulenyl)ethane unit: δ 1.33 (12H, d, $J=6.7$ Hz, $(CH_3)_2CH-7'''$, $7''''$), 2.62 (6H, s, Me- $1'''$, $1''''$), 3.00 (2H, sept, $J=6.7$ Hz, Me_2CH-7''' , $7''''$), 3.16 (6H, s, Me- $4'$, $4''$), 6.11 (2H, s, CH-1,2), 6.80 (2H, d, $J=11.0$ Hz, H- $5'''$, $5''''$), 7.21 (2H, dd, $J=11.0$, 2.3 Hz, H- $6'''$, $6''''$), 7.88 (2H, s, H- $2'''$, $2''''$) and 8.02 (2H, d, $J=2.3$ Hz, H- $8'''$, $8''''$); signals based on the 1,2-diphenyl groups: δ 6.99 (4H, dd, $J=8.0$, 7.4 Hz, H- $3'$, $3''$, $5'$, $5''$), 6.88 (2H, dd, $J=7.4$, 1.3 Hz, H- $4'$, $4''$) and 7.07 (4H, dd, $J=8.0$, 1.3 Hz, H- $2'$, $2''$, $6'$, $6''$); 176 MHz ^{13}C NMR (CD_2Cl_2), δ 146.0 (C- $1'$, $1''$), 144.8 (C- $4'''$, $4''''$), 139.3 (C- $7'''$, $7''''$), 138.7 (C- $2'''$, $2''''$), 137.7 (C- $3a'''$, $3a''''$), 134.2 (C- $6'''$, $6''''$), 133.2 (C- $8'''$, $8''''$), 131.9 (C- $1'''$, $1''''$), 129.7 (C- $3'''$, $3''''$), 129.4 (C- $2'$, $2''$, $6'$, $6''$), 127.7 (C- $3'$, $3''$, $5'$, $5''$), 126.5 (C- $5'''$, $5''''$), 125.2 (C- $4'$, $4''$), 124.9 (C- $8a'''$, $8a''''$), 53.9 (C-1,2), 37.6 (Me_2CH-7''' , $7''''$), 28.2 (Me- $4'''$, $4''''$), 24.3 ($(CH_3)_2CH-7'''$, $7''''$) and 13.0 (Me- $1'''$, $1''''$).

11b: 700 MHz 1H NMR (CD_2Cl_2), signals based on the 1,2-di(3-guaiazulenyl)ethane unit: δ 1.30, 1.31 (6H each, d, $J=7.0$ Hz, $(CH_3)_2CH-7'''$, $7''''$), 2.50 (6H, s, Me- $1'''$, $1''''$), 2.97 (2H, sept, $J=7.0$ Hz, Me_2CH-7''' , $7''''$), 3.02 (6H, s, Me- $4'''$, $4''''$), 5.81 (2H, s, CH-1,2), 6.74 (2H, d, $J=10.7$ Hz, H- $5'''$, $5''''$), 7.20 (2H, dd, $J=10.7$, 2.0 Hz, H- $6'''$, $6''''$), 7.92 (2H, s, H- $2'''$, $2''''$) and 7.97 (2H, d, $J=2.0$ Hz, H- $8'''$, $8''''$); signals based on the 1,2-diphenyl groups: δ 6.79 (4H, dd, $J=8.0$, 1.5 Hz, H- $2'$, $2''$, $6'$, $6''$), 7.01 (2H, dd, $J=7.4$, 1.5 Hz, H- $4'$, $4''$) and 7.02 (4H, dd, $J=8.0$, 7.4 Hz, H- $3'$, $3''$, $5'$, $5''$); 176 MHz ^{13}C NMR (CD_2Cl_2), δ 145.9 (C- $1'$, $1''$), 145.1 (C- $4'''$, $4''''$), 139.5 (C- $7'''$, $7''''$), 138.9 (C- $2'''$, $2''''$), 138.3 (C- $3a'''$, $3a''''$), 134.6 (C- $6'''$, $6''''$), 133.3 (C- $8'''$, $8''''$), 133.0 (C- $1'''$, $1''''$), 129.9 (C- $3'''$, $3''''$), 129.8 (C- $2'$, $2''$, $6'$, $6''$), 127.6 (C- $3'$, $3''$, $5'$, $5''$), 126.6 (C- $5'''$, $5''''$), 125.0 (C- $4'$, $4''$), 124.2 (C- $8a'''$, $8a''''$), 51.2 (C-1,2), 37.6 (Me_2CH-7''' , $7''''$), 28.0 (Me- $4'''$, $4''''$), 24.3 ($(CH_3)_2CH-7'''$, $7''''$) and 13.0 (Me- $1'''$, $1''''$).

3.1.9. Reduction of phenyl-3-guaiazulenylmethylum tetrafluoroborate (7a) with $NaBH_4$. To a solution of

$NaBH_4$ (10 mg, 270 μ mol) in ethanol (2 mL) was added a solution of **7a** (50 mg, 130 μ mol) in acetonitrile (2 mL). The mixture was stirred at 25°C for 20 min under aerobic conditions and then evaporated in vacuo. The residue thus obtained was dissolved in hexane and filtered. The hexane filtrate was evaporated in vacuo, giving pure 3-guaiazulenylmethylbenzene (**12**) as a blue paste (47 mg, 94% yield).

12: $R_f=0.43$ on silica-gel TLC (hexane); UV–Vis λ_{max} (hexane) nm (log ϵ), 246 (4.27), 289 (4.50), 306sh (4.08), 353 (3.67), 370 (3.62), 623 (2.47), 675sh (2.37) and 753sh (1.88); EI-MS (70 eV), m/z 288 (M^+ , 100%), 273 ($[M-Me]^+$, 55), 245 ($[M-i-Pr]^+$, 8), 213 ($[M-i-Pr-2Me-2H]^+$, 80), 211 ($[M-Ph]^+$, 15), 155 ($[1-i-Pr]^+$, 10), 91 ($[M-Gu^3]^+$, 15) and 77 (Ph^+ , 6); exact EI-MS (70 eV), found: m/z 288.1870; calcd for $C_{22}H_{24}$: M^+ , m/z 288.1878; 500 MHz 1H NMR (CD_3CN), signals based on the 3-guaiazulenylmethyl group: δ 1.28 (6H, d, $J=7.0$ Hz, $(CH_3)_2CH-7'$), 2.54 (3H, s, Me- $1'$), 2.76 (3H, s, Me- $4'$), 3.00 (1H, sept, $J=7.0$ Hz, Me_2CH-7'), 4.55 (2H, s, CH_2-3'), 6.79 (1H, d, $J=11.0$ Hz, H- $5'$), 7.25 (1H, dd, $J=11.0$, 2.0 Hz, H- $6'$), 7.36 (1H, s, H- $2'$) and 8.08 (1H, d, $J=2.0$ Hz, H- $8'$); signals based on the phenyl group: δ 6.97 (2H, dd, $J=8.0$, 1.5 Hz, H-2,6), 7.11 (1H, dddd, $J=7.5$, 7.5, 1.5, 1.5 Hz, H-4) and 7.21 (2H, ddd, $J=8.0$, 7.5, 1.5 Hz, H-3,5); DPV (E_p), +0.69 and –1.76 V; CV, +0.69 (E_{pa}) and –1.78 ($E_{1/2}$) V under the same electrochemical conditions as **2**.

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10. **1**: DPV (E_p), +0.65 and -1.77 V, CV, +0.69 (E_{pa}) and -1.79 ($E_{1/2}$) V under the same electrochemical conditions as **2**.
11. The potential of the E_{pa} (V) is included in the half-wave potential of -1.85 ($E_{1/2}$) V.
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