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Preparation, Structures, and Properties of New Monocarbenium Ion Compounds Stabilized by a 3-Guaiazulenyl Group and an Azobenzene Unit: Comparative Studies on Three Delocalized π-Electron Systems

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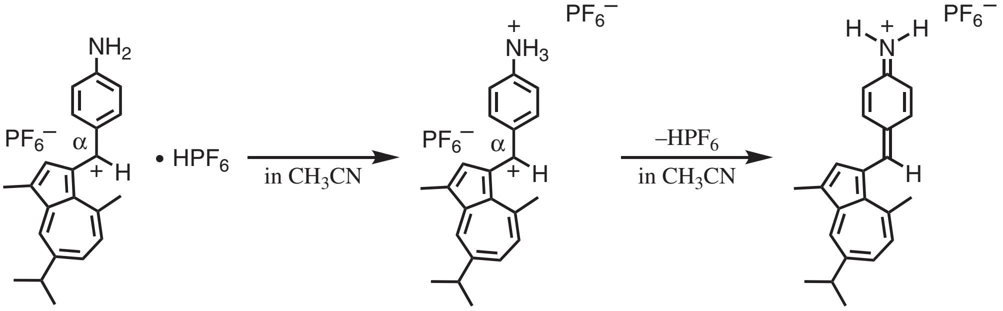
Reaction of guaiazulene (=7-isopropyl-1,4-dimethylazulene) with 4′-hydroxyazobenzene-4-carbaldehyde in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gives as high as 94% yield of a new monocarbenium ion compound (3-guaiazulenyl)[4-(4-hydroxyphenylazo)phenyl]methylium hexafluorophosphate. Similarly, reactions of guaiazulene with 4′-methoxyazobenzene-4-carbaldehyde and 4′-(dimethylamino)azobenzene-4-carbaldehyde under the same reaction conditions as the above afford the corresponding new (3-guaiazulenyl)[4-(4-methoxyphenylazo)-phenyl]methylium and {4-[4-(dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium hexafluorophosphates in 97 and 95% yields. Along with an efficient preparation of the target monocarbenium ion compounds, comparative studies on spectroscopic, chemical, and electrochemical properties of the unique products, indicating different delocalized π-electron systems, are reported. Moreover, crystal structure of {4-[4-(dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium tetrafluoroborate with an equiv of HBF_4 molecule is documented.

As a series of basic studies on creation of novel functional materials with a 3-guaiazulenyl (=5-isopropyl-3,8-dimethylazulen-1-yl) (or another azulen-1-yl) group possessing a large dipole moment and on their potential utility, we have been working on facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of delocalized mono- and dicarbenium ion compounds stabilized by extended π-electron systems possessing a 3-guaiazulenyl [or an azulen-1-yl or a 3-(methoxycarbonyl)azulen-1-yl] group.[1–18] The products, with a 3-guaiazulenyl group, can be readily (and quantitatively) obtained by the reactions of naturally occurring guaiazulene[19] (=7-isopropyl-1,4-dimethylazulene) (**1**) with the corresponding aromatic (and π-conjugated aliphatic) aldehydes in methanol in the presence of hexafluorophosphoric acid (and tetrafluoroboric acid) in comparison with other azulenes.[15,17] During the course of our basic and systematic investigations, we found that the reaction of **1** with 4-aminobenzaldehyde in CH_3OH in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave (4-aminophenyl)(3-guaiazulenyl)methylium hexafluorophosphate (**16**), with an equiv of HPF_6, in 56% yield. The elemental analysis and the IR spectrum suggested the formation of **16**, with an equiv of molecular HPF_6, forming a non-protonated H_2N-4 group in the solid state, while the ^1H, ^{19}F, and ^{31}P NMR spectra indicated the formation of the protonated **17** in CH_3CN (Chart 1).[20] Interestingly, a solution of the obtained monocarbenium ion compound **17**, forming a protonated amino group ($4\text{-}H_3N^+PF_6^-$), in CH_3CN was allowed to stand at room temperature for 48 h, gradually converting to 4-(3-guaiazulenyl)methylene-2,5-cyclohexadiene-1-iminium hexafluorophosphate (**18**), completely (Chart 1).[20] From the structures of the resulting products **16–18**, it could be inferred that the



16 **17** **18**

Chart 1.

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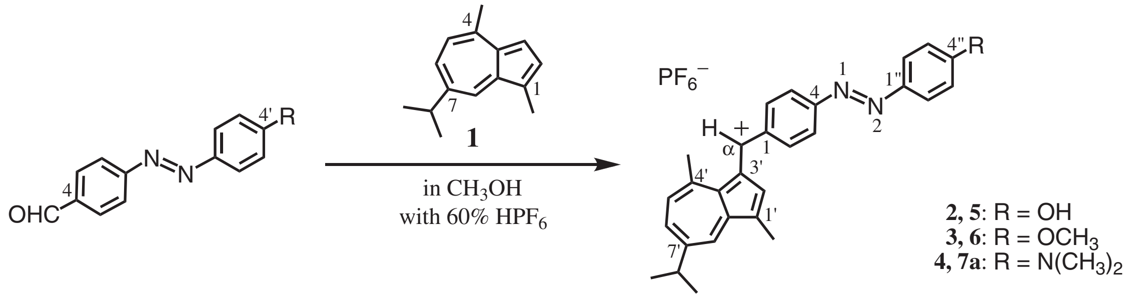
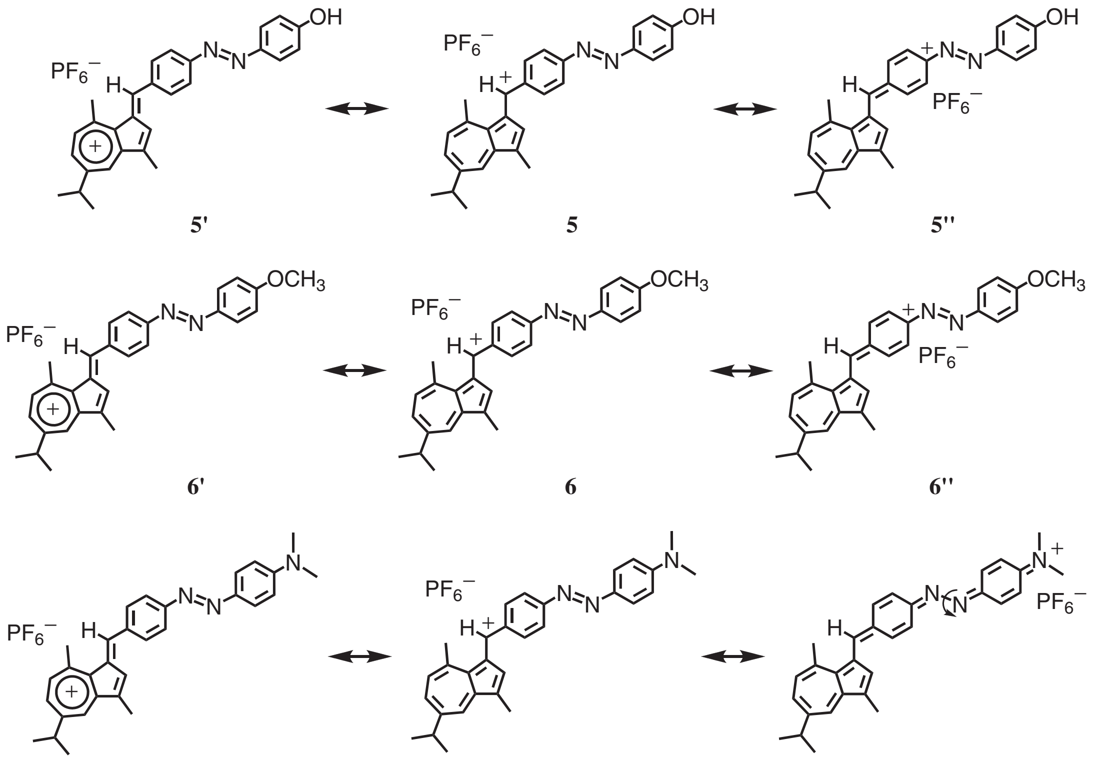


2–4

5–7a

Scheme 1. The reactions of **1** with **2–4** in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h, yielding the corresponding monocarbenium ion compounds **5–7a**.



5' **5** **5''**

6' **6** **6''**

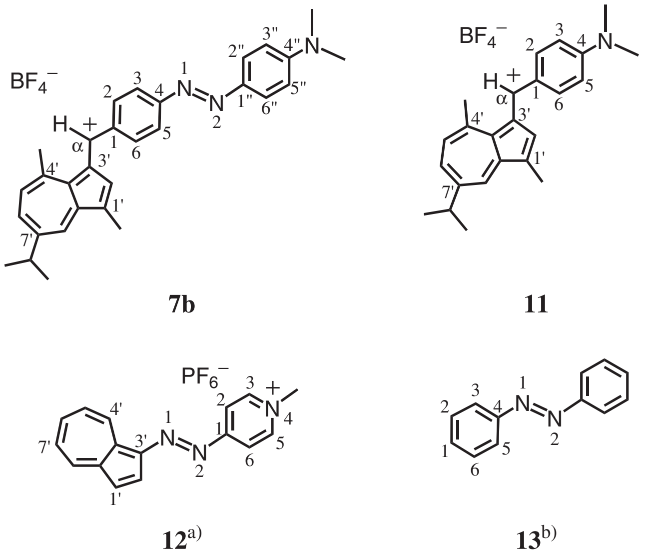
7a' **7a** **7a''**

Chart 2.

obtained **17**, forming a 4-$H_3N^+PF_6^-$ in CH_3CN, owing to the kinetic control was converted to the stabilized **18** owing to the thermodynamic control (i.e., stability of conjugated π-electron system) in the solvent.[20] In relation to the above investigations on structures and properties, our interest has quite recently been focused on the title chemistry: namely, on the reactions of **1** with azobenezene derivatives possessing an aldhyde group, i.e., **2**, **3**, and **4**[21–24] (Scheme 1), in methanol in the presence of hexafluorophosphoric acid at 25 °C, expectantly producing the corresponding new extended (and delocalized) monocarbenium ion compounds **5**, **6**, and **7a** with similar resonance structures of the 3-guaiazulenylium ion and *p*-benzoquinoid structures to those of **16**, **17**, and **18** (Charts 1 and 2). On the other hand, azobenzenes in general are currently drawing an increasing interest from the viewpoint of potential utilities as photo-memories,[25,26] optical switchings,[27–29] and optoelectronics.[30,31] We now wish to report a facile preparation as well as the spectroscopic, chemical, and electrochemical properties of the unique products **5–7a**, indicating an apparently difference between the delocalized π-electron system of **7a** and those of **5** and **6** (Chart 2), along with the crystal structure of the monocarbenium tetrafluoroborate **7b** compared with those of structurally related known compounds **11–13** (Chart 3).

Experimental

General. Thermal (TGA and DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder. 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. NMR spectra were recorded with a JEOL GX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) and JNM-ECA600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) cryospectrometer. ^{1}H NMR spectra (δ and *J* values) were assigned



7b **11** **12**[a)] **13**[b)]

Chart 3. a) For a comparative purpose, the numbering scheme of the 1-azulenyl group of **12** was changed to that of the 3-azulenyl group. b) For a comparative purpose, the numbering scheme of the phenyl group of **13** was changed to that of the 4-phenyl group.

using computer-assisted simulation (software: gNMR developed by Adept Scientific plc) on a SONY VAIO PCV-HS80 personal computer with a Pentium (R) 4 processor. Cyclic and differential pulse voltammograms were measured with an ALS Model 600 electrochemical analyzer.

Preparation of 4′-Hydroxyazobenzene-4-carbaldehyde (2). Compound 2 was prepared according to procedures based on reference No. 23: namely, to a solid of 4-aminobenzaldehyde (50 mg, 412 μmol) was added an aqueous solution (0.15 mL) of 12% HCl at −15 °C and further an aqueous solution (2.0 mL) of $NaNO_2$ (50 mg, 724 μmol) was added to the above solution. The mixture was stirred for 15 min, yielding the corresponding diazonium salt. An aqueous solution (2.0 mL) of phenol (40 mg, 425 μmol) was then added to the aqueous solution of the diazonium salt, turning the orange solution red, and the mixture was further stirred at room temperature for 30 min. After the reaction, the solution was carefully neutralized with aq $NaHCO_3$ and then the mixture was extracted with dichloromethane (10 mL × 3). The extract was washed with distilled water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate–benzene (60:30:10, v/v/v) as an eluant. The crude product **2** was recrystallized from hexane (several times) to provide pure **2** as stable crystals (77 mg, 340 μmol, 83% yield).

Compound **2**:[22] Yellow prisms, $R_f = 0.22$ on silica gel TLC (hexane–EtOAc–benzene = 60:30:10, v/v/v); exact EI-MS (70 eV), found: *m/z* 226.0737 (M^+, 100%); calcd for $C_{13}H_{10}O_2N_2$: M^+, *m/z* 226.0742.

Preparation of 4′-Methoxyazobenzene-4-carbaldehyde (3). Compound **3** was prepared according to procedures described in reference No. 23: namely, a solution of **2** (80 mg, 353 μmol) in acetone (5.0 mL) was added to a suspension of K_2CO_3 (50 mg, 361 μmol) in acetone (5.0 mL) and further a solution of CH_3I (80 μL, 781 μmol) was added to the above solution. The mixture was refluxed for 2 h under argon. After cooling to room temperature, the solvent was evaporated in vacuo and then the residue was dissolved in dichloromethane (30 mL), which was washed with distilled water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate–benzene (80:15:5, v/v/v) as an eluant. The crude product **3** was recrystallized from hexane (several times) to provide pure **3** as stable crystals (59 mg, 245 μmol, 69% yield).

Compound **3**:[22] Orange needles, $R_f = 0.28$ on silica gel TLC (hexane–AcOEt–benzene = 80:15:5, v/v/v); exact EI-MS (70 eV), found: *m/z* 240.0901 (M^+, 100%); calcd for $C_{14}H_{12}O_2N_2$: M^+, *m/z* 240.0899.

Preparation of 4′-(Dimethylamino)azobenzene-4-carbaldehyde (4). Compound **4** was prepared according to the procedures reported in references No. 22 and 23: namely, to a solid of 4-aminobenzaldehyde (50 mg, 412 μmol) was added an aqueous solution (0.15 mL) of 12% HCl at −15 °C and further an aqueous solution (2.0 mL) of $NaNO_2$ (50 mg, 724 μmol) was added to the above solution. The mixture was stirred for 15 min, yielding the corresponding diazonium salt and then a solution of *N*,*N*-dimethylaniline (60 μL, 495 μmol) was added to the aqueous solution of the diazonium salt, turning the orange solution red, the mixture was further stirred at room temperature for 30 min. After the reaction, the solution was carefully neutralized with aq $NaHCO_3$ and then the mixture was extracted with dichloromethane (10 mL × 3). The extract was washed with distilled water, dried ($MgSO_4$), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (80:20, v/v) as an eluant. The crude product **4** was recrystallized from hexane–dichloromethane (90:10, v/v) (several times) to provide pure **4** as stable crystals (80 mg, 315 μmol, 76% yield).

Compound **4**:[23] Red prisms, $R_f = 0.44$ on silica gel TLC (hexane–AcOEt = 80:20, v/v); exact EI-MS (70 eV), found: *m/z* 253.1236 (M^+, 100%); calcd for $C_{15}H_{15}ON_3$: M^+, *m/z* 253.1215.

Preparation of (3-Guaiazulenyl)[4-(4-hydroxyphenylazo)-phenyl]methylium Hexafluorophosphate (5). To a solution of commercially available guaiazulene (**1**) (30 mg, 151 μmol) in methanol (1.0 mL) was added a solution of 4′-hydroxyazobenzene-4-carbaldehyde (**2**) (30 mg, 132 μmol) in methanol (3.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.15 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-green solid of **5** and then was centrifuged at 2.5 krpm for 1 min. The crude product **5** thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (10:50, v/v) (several times) to provide pure **5** as a red powder (69 mg, 124 μmol, 94% yield).

Compound **5**: Red powder, mp >180 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 61.01; H, 4.64; N, 5.03%. Calcd for $C_{28}H_{27}ON_2F_6P$: C, 60.87; H, 4.93; N, 5.07%; UV–vis λ_{max} (CH_3CN) nm (log ε), 232 (4.47), 343 (4.29), and 498 (4.56); IR ν_{max} (KBr) cm^{-1}, 3503 (O–H), 1601 (N=N), and 841, 559 (PF_6^-); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: *m/z* 407.2101; calcd for $C_{28}H_{27}ON_2$: $[M - PF_6]^+$, *m/z* 407.2124; 500 MHz ^1H NMR (CD_3CN): signals based on a 3-guaiazulenylmethylium substituent: δ 1.45 (6H, d, $J = 6.9$ Hz, $(CH_3)_2CH$-7′), 2.50 (3H, s, Me-1′), 3.33 (3H, s, Me-4′), 3.47 (1H, sept, $J = 6.9$ Hz, Me_2CH-7′), 7.95 (1H, s, H-2′), 8.38 (1H, dd, $J = 11.0$, 2.3 Hz, H-6′), 8.48 (1H, d, $J = 11.0$ Hz, H-5′), 8.53 (1H, d, $J = 2.3$ Hz, H-8′), and 8.69 (1H, s, HC^+-α); signals based on a 4-(4-hydroxyphenylazo)benzene part: δ 6.90 (2H, ddd, $J = 8.9$, 3.1, 2.0 Hz, H-3″,5″), 7.69 (1H, s, HO-4″), 7.78 (2H, ddd, $J = 8.9$, 3.1, 2.0 Hz, H-2″,6″), 7.90 (2H, ddd, $J = 8.7$, 2.3, 1.4 Hz, H-2,6), and 7.94 (2H, ddd, $J = 8.7$, 2.3, 1.4 Hz, H-3,5); 125 MHz ^{13}C NMR (CD_3CN): δ 172.1 (C-7′), 161.9 (C-4″), 161.6 (C-8a′), 158.0 (C-4′), 154.8 (C-4), 153.6 (C-3a′), 150.9 (C-5′), 148.9 (HC$^+$-α), 147.4 (C-1″), 146.7 (C-1′), 145.1 (C-6′), 141.1 (C-2′), 140.9 (C-3′), 139.8 (C-8′), 138.0 (C-1), 135.0 (C-2,6), 126.3 (C-2″,6″), 124.0 (C-3,5), 116.9 (C-3″,5″), 40.2 (Me_2CH-7′), 29.7 (Me-4′), 23.7 ($(CH_3)_2$CH-7′), and 13.9 (Me-1′).

Preparation of (3-Guaiazulenyl)[4-(4-methoxyphenylazo)phenyl]methylium Hexafluorophosphate (6). To a solution of guaiazulene (**1**) (30 mg, 151 µmol) in methanol (1.0 mL) was added a solution of 4′-methoxyazobenzene-4-carbaldehyde (**3**) (30 mg, 124 µmol) in methanol (3.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.15 mL). The mixture was stirred at 25 °C for 2 h, precipitating a red solid of **6** and then was centrifuged at 2.5 krpm for 1 min. The crude product **6** thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (10:50, v/v) (several times) to provide pure **6** as stable crystals (68 mg, 120 µmol, 97% yield).

Compound **6**: Red blocks, mp >132 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 61.41; H, 4.94; N, 5.02%. Calcd for $C_{29}H_{29}ON_2F_6P$: C, 61.48; H, 5.16; N, 4.94%; UV–vis λ_{max} (CH_3CN) nm (log ε), 232 (4.50), 346 (4.33), and 496 (4.58); IR ν_{max} (KBr) cm^{-1}, 1601 (N=N) and 837, 556 (PF_6^-); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 421.2305; calcd for $C_{29}H_{29}ON_2$: $[M - PF_6]^+$, m/z 421.2280; 600 MHz ^{1}H NMR (CD_3CN): signals based on a 3-guaiazulenylmethylium substituent: δ 1.45 (6H, d, $J = 6.9$ Hz, $(CH_3)_2$CH-7′), 2.51 (3H, s, Me-1′), 3.35 (3H, s, Me-4′), 3.48 (1H, sept, $J = 6.9$ Hz, Me_2CH-7′), 7.98 (1H, s, H-2′), 8.41 (1H, dd, $J = 11.2$, 2.5 Hz, H-6′), 8.51 (1H, d, $J = 11.2$ Hz, H-5′), 8.56 (1H, d, $J = 2.5$ Hz, H-8′), and 8.74 (1H, s, HC$^+$-α); signals based on a 4-(4-methoxyphenylazo)benzene part: δ 3.88 (3H, s, MeO-4″), 7.06 (2H, ddd, $J = 8.9$, 3.0, 2.0 Hz, H-3″,5″), 7.91 (2H, ddd, $J = 8.9$, 3.0, 2.0 Hz, H-2″,6″), 7.94 (2H, ddd, $J = 8.3$, 2.2, 1.9 Hz, H-2,6), and 7.99 (2H, ddd, $J = 8.3$, 2.2, 1.9 Hz, H-3,5); 150 MHz ^{13}C NMR (CD_3CN): δ 172.2 (C-7′), 164.1 (C-4″), 161.7 (C-8a′), 158.2 (C-4′), 154.9 (C-4), 153.7 (C-3a′), 151.0 (C-5′), 149.0 (HC$^+$-α), 147.9 (C-1″), 146.7 (C-1′), 145.1 (C-6′), 141.2 (C-2′), 141.0 (C-3′), 139.9 (C-8′), 138.2 (C-1), 135.0 (C-2,6), 126.1 (C-2″,6″), 124.0 (C-3,5), 115.6 (C-3″,5″), 56.5 (MeO-4″), 40.3 (Me_2CH-7′), 29.7 (Me-4′), 23.7 ($(CH_3)_2$CH-7′), and 13.9 (Me-1′).

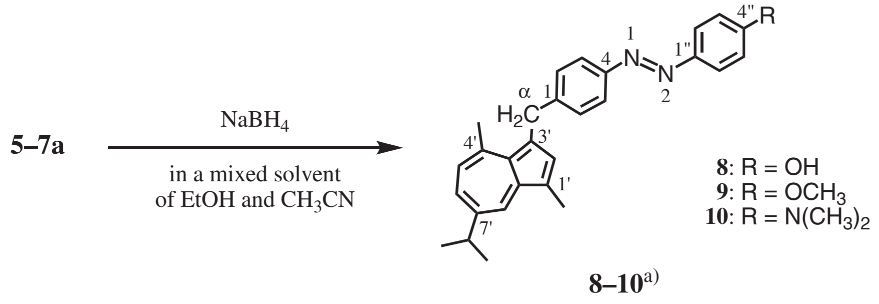
Preparation of {4-[4-(Dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium Hexafluorophosphate (7a). To a solution of guaiazulene (**1**) (30 mg, 151 µmol) in methanol (1.0 mL) was added a solution of 4′-(dimethylamino)azobenzene-4-carbaldehyde (**4**) (30 mg, 118 µmol) in methanol (3.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.15 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-blue solid of **7a** and then was centrifuged at 2.5 krpm for 1 min. The crude product **7a** thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (10:50, v/v) (several times) to provide pure **7a** as stable crystals (65 mg, 112 µmol, 95% yield).

Compound **7a**: Green plates, mp >140 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 62.03; H, 5.23; N, 6.94%. Calcd for $C_{30}H_{32}N_3F_6P$: C, 62.17; H, 5.57; N, 7.25%; UV–vis λ_{max} (CH_3CN) nm (log ε), 233 (4.42), 414 (4.22), and 600 (4.74); IR ν_{max} (KBr) cm^{-1}, 1620 (N=N) and 841, 559 (PF_6^-); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 434.2570; calcd for $C_{30}H_{32}N_3$: $[M - PF_6]^+$, m/z 434.2596; 500 MHz ^{1}H NMR (CD_3CN): signals based on a 3-guaiazulenylmethylium substituent: δ 1.45 (6H, d, $J = 7.0$ Hz, $(CH_3)_2$CH-7′), 2.53 (3H, s, Me-1′), 3.36 (3H, s, Me-4′), 3.49 (1H, sept, $J = 7.0$ Hz, Me_2CH-7′), 8.04 (1H, s, H-2′), 8.41 (1H, dd, $J = 11.0$, 2.3 Hz, H-6′), 8.51 (1H, d, $J = 11.0$ Hz, H-5′), 8.59 (1H, d, $J = 2.0$ Hz, H-8′), and 8.73 (1H, s, HC$^+$-α); signals based on a 4-[4-(dimethylamino)phenylazo]benzene part: δ 3.48 (6H, s, Me_2N-4″), 7.85 (2H, ddd, $J = 9.0$, 2.2, 1.7 Hz, H-3,5), and 7.98 (2H, ddd, $J = 9.0$, 2.2, 1.7 Hz, H-2,6); 125 MHz ^{13}C NMR (CD_3CN): δ 172.5 (C-7′), 162.0 (C-8a′), 158.9 (C-4′), 154.5 (C-3a′), 151.5 (C-5′), 149.9 (HC$^+$-α), 147.3 (C-1′), 145.9 (C-6′), 142.0 (C-2′), 141.1 (C-3′), 140.8 (C-8′), 136.9 (C-2,6), 120.1 (C-3,5), 44.4 (Me_2N-4″), 41.2 (Me_2CH-7′), 30.7 (Me-4′), 24.7 ($(CH_3)_2$CH-7′), and 14.8 (Me-1′).

Reduction of (3-Guaiazulenyl)[4-(4-hydroxyphenylazo)phenyl]methylium Hexafluorophosphate (5) with $NaBH_4$. To a solution of $NaBH_4$ (11 mg, 290 µmol) in ethanol (2.0 mL) was added a solution of **5** (40 mg, 72 µmol) in acetonitrile (2.0 mL). The mixture was stirred at 25 °C for 30 min and then was evaporated in vacuo. The residue thus obtained was dissolved in hexane (5.0 mL), and was filtered. The filtrate was evaporated in vacuo, giving a green pasty residue, which was carefully separated by silica gel column chromatography with hexane–ethyl acetate (80:20, v/v) as an eluant. The separated product **8** was recrystallized from hexane (several times) to provide pure 4-(3-guaiazulenylmethyl)-4′-hydroxyazobenzene as a green powder (25 mg, 61 µmol, 85% yield).

Compound **8**: Green powder, mp 155 °C [determined by thermal analysis (TGA and DTA)]. $R_f = 0.22$ on silica gel TLC (hexane–AcOEt = 80:20, v/v); UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 246 (4.58), 293 (4.70), 352 (4.56), and 620 (2.76); IR ν_{max} (KBr) cm^{-1}, 3414 (O–H) and 1593 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 408.2190; calcd for $C_{28}H_{28}ON_2$: M^+, m/z 408.2201; 600 MHz ^{1}H NMR (CD_3CN): signals based on a 3-guaiazulenylmethyl group: δ 1.31 (6H, d, $J = 6.9$ Hz, $(CH_3)_2$CH-7′), 2.58 (3H, s, Me-1′), 2.80 (3H, s, Me-4′), 3.03 (1H, sept, $J = 6.9$ Hz, Me_2CH-7′), 4.65 (2H, s, H_2C-3′), 6.82 (1H, d, $J = 10.7$ Hz, H-5′), 7.31 (1H, dd, $J = 10.7$, 2.3 Hz, H-6′), 7.42 (1H, s, H-2′), and 8.13 (1H, d, $J = 2.3$ Hz, H-8′); signals based on a 4-hydroxyazobenzene part: δ 6.93 (2H, ddd, $J = 8.9$, 2.7, 2.0 Hz, H-3″,5″), 7.15 (2H, ddd, $J = 8.2$, 2.4, 1.7 Hz, H-2,6), 7.57 (1H, s, HO-4″), 7.71 (2H, ddd, $J = 8.2$, 2.4, 1.7 Hz, H-3,5), and 7.76 (2H, ddd, $J = 8.9$, 2.7, 2.0 Hz, H-2″,6″); 150 MHz ^{13}C NMR (CD_3CN): δ 160.8 (C-4″), 151.7 (C-4), 147.5 (C-1), 147.3 (C-1″), 146.3 (C-4′), 141.9 (C-2′), 140.2 (C-7′), 138.8 (C-8a′), 135.9 (C-6′), 134.4 (C-8′), 133.8 (C-3a′), 130.0 (C-2,6), 127.1 (C-5′), 126.1 (C-3′), 125.5 (C-2″,6″), 125.3 (C-1′), 123.3 (C-3,5), 116.7 (C-3″,5″), 38.3 (Me_2CH-7′), 37.4 (H_2C-3′), 26.8 (Me-4′), 24.7 ($(CH_3)_2$CH-7′), and 12.9 (Me-1′). For comparative purposes on ^{1}H and ^{13}C NMR signals, the numbering scheme of compound **8** was changed as shown in Scheme 2.

Reduction of (3-Guaiazulenyl)[4-(4-methoxyphenylazo)phenyl]methylium Hexafluorophosphate (6) with $NaBH_4$. To a solution of $NaBH_4$ (11 mg, 290 µmol) in ethanol (2.0 mL) was added a solution of **6** (40 mg, 70 µmol) in acetonitrile (2.0 mL). The mixture was stirred at 25 °C for 30 min and then was evaporated in vacuo. The residue thus obtained was dissolved in hexane (5.0 mL), and was filtered. The filtrate was evaporated in vacuo, giving a green pasty residue, which was carefully separated by silica gel column chromatography with hexane–ethyl acetate (90:10, v/v) as an eluant. The separated product **9** was recrystallized from hexane (several times) to provide pure 4-(3-guaiazulenylmethyl)-4′-methoxyazobenzene as green blocks (22 mg, 52 µmol, 74% yield).



Scheme 2. The reductions of **5–7a** with $NaBH_4$ in a mixed solvent of EtOH and CH_3CN at 25 °C for 30 min, yielding the corresponding hydride-reduction products **8–10**. a) For a comparative purposes on ^1H and ^{13}C NMR signals, the numbering schemes of compounds **8–10** were changed as shown in Scheme 2.

Compound **9**: Green blocks, mp 122 °C [determined by thermal analysis (TGA and DTA)]. $R_f = 0.30$ on silica gel TLC (hexane–EtOAc = 90:10, v/v); UV–vis λ_{max} (CH_2Cl_2) nm ($\log \varepsilon$), 246 (4.57), 293 (4.69), 353 (4.55), and 618 (2.74); IR ν_{max} (KBr) cm^{-1}, 1601 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 422.2388; calcd for $C_{29}H_{30}ON_2$: M^+, m/z 422.2358; 600 MHz ^1H NMR (CD_3CN): signals based on a 3-guaiazulenylmethyl group: δ 1.31 (6H, d, $J = 6.8$ Hz, $(CH_3)_2CH$-7′), 2.58 (3H, s, Me-1′), 2.81 (3H, s, Me-4′), 3.03 (1H, sept, $J = 6.8$ Hz, Me_2CH-7′), 4.66 (2H, s, H_2C-3′), 6.83 (1H, d, $J = 10.8$ Hz, H-5′), 7.32 (1H, dd, $J = 10.8$, 2.0 Hz, H-6′), 7.42 (1H, s, H-2′), and 8.13 (1H, d, $J = 2.0$ Hz, H-8′); signals based on 4-methoxyazobenzene: δ 3.85 (3H, s, MeO-4″), 7.05 (2H, ddd, $J = 9.1$, 3.1, 2.2 Hz, H-3″,5″), 7.16 (2H, ddd, $J = 8.4$, 2.3, 1.9 Hz, H-2,6), 7.73 (2H, ddd, $J = 8.4$, 2.3, 1.9 Hz, H-3,5), and 7.84 (2H, ddd, $J = 9.1$, 3.1, 2.2 Hz, H-2″,6″); 150 MHz ^{13}C NMR (CD_3CN): δ 163.1 (C-4″), 151.7 (C-4), 147.8 (C-1), 147.6 (C-1″), 146.3 (C-4′), 141.9 (C-2′), 140.2 (C-7′), 138.8 (C-8a′), 135.9 (C-6′), 134.4 (C-8′), 133.8 (C-3a′), 130.0 (C-2,6), 127.2 (C-5′), 126.0 (C-3′), 125.3 (C-2″,6″), 125.3 (C-1′), 123.3 (C-3,5), 115.3 (C-3″,5″), 56.3 (MeO-4″), 38.3 (Me_2CH-7′), 37.4 (H_2C-3′), 26.8 (Me-4′), 24.7 ($(CH_3)_2CH$-7′), and 12.9 (Me-1′). For comparative purposes on ^1H and ^{13}C NMR signals, the numbering scheme of compound **9** was changed as shown in Scheme 2.

Reduction of {4-[4-(Dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium Hexafluorophosphate (7a) with $NaBH_4$. To a solution of $NaBH_4$ (10 mg, 264 µmol) in ethanol (2.0 mL) was added a solution of **7a** (40 mg, 69 µmol) in acetonitrile (2.0 mL). The mixture was stirred at 25 °C for 30 min and then was evaporated in vacuo. The residue thus obtained was dissolved in dichloromethane (5.0 mL), and was filtered. The filtrate was evaporated in vacuo, giving a green pasty residue, which was carefully separated by silica gel column chromatography with hexane–ethyl acetate (90:10, v/v) as an eluant. The separated product **10** was recrystallized from dichloromethane–acetonitrile (10:50, v/v) (several times) to provide pure 4′-dimethylamino-4-(3-guaiazulenylmethyl)azobenzene as green blocks (22 mg, 50 µmol, 72% yield).

Compound **10**: Green blocks, mp 223 °C [determined by thermal analysis (TGA and DTA)]. $R_f = 0.28$ on silica gel TLC (hexane–EtOAc = 90:10, v/v); UV–vis λ_{max} (CH_2Cl_2) nm ($\log \varepsilon$), 248 (4.54), 293 (4.71), 413 (4.55), and 620 (2.74); IR ν_{max} (KBr) cm^{-1}, 1597 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 435.2665; calcd for $C_{30}H_{33}N_3$: M^+, m/z 435.2675; 600 MHz ^1H NMR (CD_2Cl_2): signals based on a 3-guaiazulenylmethyl group: δ 1.35 (6H, d, $J = 7.0$ Hz, $(CH_3)_2CH$-7′), 2.62 (3H, s, Me-1′), 2.84 (3H, s, Me-4′), 3.03 (1H, sept, $J = 7.0$ Hz, Me_2CH-7′), 4.67 (2H, s, H_2C-3′), 6.82 (1H, d, $J = 11.0$ Hz, H-5′), 7.28 (1H, dd, $J = 11.0$, 2.0 Hz, H-6′), 7.43 (1H, s, H-2′), and 8.11 (1H, d, $J = 2.0$ Hz, H-8′); signals based on a 4-(dimethylamino)azobenzene part: δ 3.07 (6H, s, Me_2N-4″), 6.77 (2H, ddd, $J = 9.0$, 3.0, 2.0 Hz, H-3″,5″), 7.14 (2H, ddd, $J = 8.6$, 2.0, 2.0 Hz, H-2,6), 7.71 (2H, ddd, $J = 8.6$, 2.0, 2.0 Hz, H-3,5), and 7.82 (2H, ddd, $J = 9.0$, 3.0, 2.0 Hz, H-2″,6″); 150 MHz ^{13}C NMR (CD_2Cl_2): δ 152.1 (C-4″), 150.8 (C-4), 145.0 (C-4′), 144.8 (C-1), 143.1 (C-1″), 140.7 (C-2′), 138.7 (C-7′), 137.5 (C-8a′), 134.4 (C-6′), 133.0 (C-8′), 132.7 (C-3a′), 128.6 (C-2,6), 125.8 (C-5′), 124.8 (C-3′), 124.3 (C-2″,6″), 123.9 (C-1′), 121.7 (C-3,5), 111.1 (C-3″,5″), 39.8 (Me_2N-4″), 37.3 (Me_2CH-7′), 36.6 (H_2C-3′), 26.1 (Me-4′), 23.9 ($(CH_3)_2CH$-7′), and 12.2 (Me-1′). For comparative purposes on ^1H and ^{13}C NMR signals, the numbering scheme of compound **10** was changed as shown in Scheme 2.

Preparation of {4-[4-(Dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium Tetrafluoroborate (7b). To a solution of guaiazulene (**1**) (30 mg, 151 µmol) in methanol (1.0 mL) was added a solution of 4′-(dimethylamino)azobenzene-4-carbaldehyde (**4**) (30 mg, 118 µmol) in methanol (3.0 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.15 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-blue solid of **7b** and then was centrifuged at 2.5 krpm for 1 min. The crude product **7b** thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (10:50, v/v) (several times) to provide pure **7b** as stable single crystals (58 mg, 95 µmol, 81% yield) with an equiv of HBF_4 molecule.

Compound **7b**: Green plates. Found: C, 59.43; H, 5.69; N, 7.14%. Calcd for $C_{30}H_{33}N_3B_2F_8$: C, 59.15; H, 5.46; N, 6.90%.

X-ray Crystal Structure of {4-[4-(Dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium Tetrafluoroborate (7b). A total 7096 reflections with $2\theta_{max} = 55.0°$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at −75 °C. The structure was solved by direct methods (SIR92)[32] and expanded using Fourier techniques (DIRDIF94).[33] 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.[34] Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-669773 for compound No. **7b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for **7b**: $C_{30}H_{33}N_3B_2F_8$ (FW 609.22), green plate (the crystal size, $0.30 \times 0.30 \times 0.50$ mm^3), triclinic, $P\bar{1}$ (#2), $a = 10.202(2)$ Å, $b = 20.324(3)$ Å, $c = 7.249(1)$ Å, $\alpha = 99.56(1)°$, $\beta = 94.74(2)°$, $\gamma = 97.42(1)°$, $V = 1461.5(4)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.382$ g cm^{-3}, $\mu(\mathrm{Mo\,K}\alpha) = 1.16$ cm^{-1}, Scan width $= (1.21 + 0.30 \tan\theta)°$, Scan mode $= \omega$–2θ, Scan rate $= 8.0°$ min^{-1}, measured reflections = 7096, observed reflections = 6717, No. of parameters = 388, $R1 = 0.081$, $wR2 = 0.240$, and Goodness of Fit Indicator = 1.56.

Results and Discussion

Preparation and Spectroscopic Properties of 5, 6, and 7a. The target monocarbeniun ion compounds **5**, **6**, and **7a** were prepared in methanol according to the procedures shown in Scheme 1, Table 1, and Experimental Section. The structures of the products **5**–**7a** were established on the basis of elemental analysis and spectroscopic data [UV–vis, IR, exact FAB-MS, and ^{1}H and ^{13}C NMR including 2D NMR (i.e., H–H COSY, HMQC, and HMBC)].

Table 1. The Yield (%) of the Products **5**–**7a** Obtained from the Reactions of **1** with **2**–**4** in CH_3OH in the Presence of Hexafluorophosphoric Acid

Entry	Substituent R	Temp/°C	Time/h	Product	Yield/%[a]
1	OH	25	2	**5**	94
2	OCH_3	25	2	**6**	97
3	$N(CH_3)_2$	25	2	**7a**	95

a) Isolated yield.

Compound **5** was obtained as a red powder. The UV–vis spectrum is shown in Figure 1a. A comparative study of the UV–vis spectrum of **5** with that of **1** (Figure 1b) showed that the characteristic UV–vis absorption bands based on **1** were not observed, indicating the formation of the structure **5** with an extended π-electron system formed by a 3-guaiazulenylmethylium ion and a 4-hydroxyazobenzene. The longest absorption wavelength appeared at 498 nm ($\log \varepsilon = 4.56$). The IR spectrum showed four specific bands from O–H at $\nu_{\max}$ 3503 cm^{-1}, N=N at $\nu_{\max}$ 1601 cm^{-1}, and PF_6^- at $\nu_{\max}$ 841 and 559 cm^{-1}. The formula $C_{28}H_{27}ON_2$ for $[M - PF_6]^+$ ion was determined by exact FAB-MS spectrum. An elemental analysis confirmed the formula $C_{28}H_{27}ON_2F_6P$. The ^{1}H NMR spectrum showed signals originating from a 3-guaiazulenylmethylium ion structure with a resonance structure of a 3-guaiazulenylium ion, and showed signals originating from a 4-(4-hydroxyphenylazo)phenyl group, the signals of which were carefully assigned using computer-assisted simulation based on first-order analysis along with H–H COSY (Tables 2 and 3). The ^{13}C NMR spectrum exhibited 23 carbon signals assigned by HMQC and HMBC (Tables 4 and 5). Thus, the elemental analysis and the spectroscopic data for **5** led to the structure (3-guaiazulenyl)[4-(4-hydroxyphenylazo)phenyl]methylium hexafluorophosphate.

Compound **6** was obtained as red blocks. The characteristic UV–vis absorption bands coincided with those of **5** (Figure 1a). The IR spectrum showed three specific bands resulting from N=N at $\nu_{\max}$ 1601 cm^{-1} and PF_6^- at $\nu_{\max}$ 837 and 556 cm^{-1}, the wavenumbers of which coincided with those of **5**. The formula $C_{29}H_{29}ON_2$ for $[M - PF_6]^+$ ion was determined by exact FAB-MS spectrum. Elemental analysis

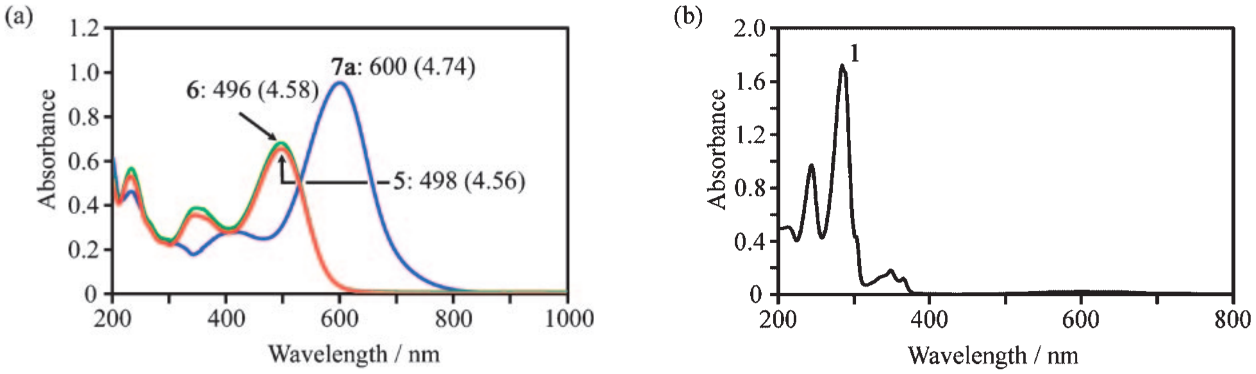


Figure 1. (a) The UV–vis spectra of **5**, **6**, and **7a** in CH_3CN. Concentrations, **5**: 0.10 g L^{-1} (181 µmol L^{-1}), **6**: 0.10 g L^{-1} (177 µmol L^{-1}), and **7a**: 0.10 g L^{-1} (173 µmol L^{-1}). Length of the cell, 0.1 cm each. $\log \varepsilon$ values are given in parenthesis. (b) The UV–vis spectrum of **1** in CH_3CN. Concentration, **1**: 0.075 g L^{-1} (379 µmol L^{-1}). Length of the cell, 0.1 cm. **1**: $\lambda_{\max}$/nm ($\log \varepsilon$), 213 (4.10), 244 (4.39), 284 (4.61), 301sh (4.03), 348 (3.65), 365 (3.46), 600 (2.68), 648sh (2.61), and 721sh (2.20).

Table 2. The ^{1}H NMR Chemical Shifts (δ) for the 3-Guaiazulenylmethylium Ions of **5**–**7a** and the 3-Guaiazulenylmethyl Groups of **8**–**10** in CD_3CN at 25 °C

Compound	HC-α	Me-1′	H-2′	Me-4′	H-5′	H-6′	Me_2CH-7′	$(CH_3)_2CH$-7′	H-8′
5	8.69	2.50	7.95	3.33	8.48	8.38	3.47	1.45	8.53
6	8.74	2.51	7.98	3.35	8.51	8.41	3.48	1.45	8.56
7a	8.73	2.53	8.04	3.36	8.51	8.41	3.49	1.45	8.59
8	4.65[a]	2.58	7.42	2.80	6.82	7.31	3.03	1.31	8.13
9	4.66[a]	2.58	7.42	2.81	6.83	7.32	3.03	1.31	8.13
10[b]	4.67[a]	2.62	7.43	2.84	6.82	7.28	3.03	1.35	8.11

a) H_2C-3′. b) Measurement solvent: CD_2Cl_2.

confirmed the formula $C_{29}H_{29}ON_2F_6P$. The ^{1}H NMR spectrum showed signals from a 3-guaiazulenylmethylium ion with a resonance structure of a 3-guaiazulenylium ion, and displayed signals from a 4-(4-methoxyphenylazo)phenyl group, the signals of which were carefully assigned using similar techniques to those of **5** (Tables 2 and 3). The ^{13}C NMR spectrum exhibited 24 carbon signals assigned by HMQC and HMBC (Tables 4 and 5). Thus, the elemental analysis and the spectroscopic data for **6** led to the structure (3-guaiazulenyl)[4-(4-methoxyphenylazo)phenyl]methylium hexafluorophosphate.

Compound **7a** was obtained as green plates. The UV–vis spectrum showed that the spectral pattern of **7a** resembled those of **5** and **6**; however, the longest absorption wavelength of **7a** showed a large bathochromic shift (Δ102 and 104 nm) and a large hyperchromic effect ($\Delta \log \varepsilon = 0.18$ and 0.16) in comparison with those of **5** and **6** (Figure 1a). The IR spectrum showed three specific bands from N=N at $\nu_{\max}$ 1620 cm^{-1}, which was higher than those of **5** and **6**, and PF_6^- at $\nu_{\max}$ 841 and 559 cm^{-1}, which coincided with those of **5** and **6**. The formula $C_{30}H_{32}N_3$ for $[M - PF_6]^+$ ion was determined by exact FAB-MS spectrum. Elemental analysis confirmed the formula $C_{30}H_{32}N_3F_6P$. The ^{1}H NMR spectrum showed signals from a 3-guaiazulenylmethylium ion structure with a resonance structure of a 3-guaiazulenylium ion, and revealed three signals orginating from the H-2,6, H-3,5, and Me$_2$N-4″ protons of a 4-[4-(dimethylamino)phenylazo]phenyl group, the signals of which were carefully assigned using similar techniques to those of **5** (Tables 2 and 3). Furthermore, the broadened signals resulting from the H-2″,6″ and H-3″,5″ protons were observed at 25 °C (Figure 2), and could not be unambiguously assigned. The ^{13}C NMR spectrum exhibited 18 carbon signals assigned by HMQC and HMBC (Tables 4 and 5); however, the six signals from the C-1, C-4, C-1″, C-2″,6″, C-3″,5″, and C-4″ carbons were not observed. The ^{1}H and ^{13}C NMR spectral data suggested the existence of rotational stereoisomers for **7a″** at 25 °C (Chart 2). Then, along with the above analyses, the variable-temperature ^{1}H NMR spectra of **7a** in CD$_3$CN at 70, 40, 25, 0, and −40 °C were measured (Figure 2). As a result, it was found that the H-2″,6″ and H-3″,5″ proton signals were not observed completely at 0 °C and corresponding broadened signals were observed at 25 and 40 °C. However, two signals (δ 7.92 and 7.28 for the H-2″,6″ and H-3″,5″ protons) were observed at 70 °C and four signals (δ 7.96, 7.69, 7.27, and 7.08 for the H-2″, 6″, 3″, and 5″ protons) were observed at −40 °C. These results support the formation of rotational stereoisomers of **7a″** under the measurement conditions. All the signals observed at −40 °C showed up-field shifts in comparison with those observed at other temperatures, resulting from the difference between the ring-current effect of the yielded rotational stereoisomers. Thus, the elemental analysis and the spectroscopic data for **7a** led to the structure {4-[4-(dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium hexafluorophosphate.

Table 3. The ^{1}H NMR Chemical Shifts (δ) for the Azobenzenes of **5**–**10** in CD$_3$CN at 25 °C

Compound	H-2,6	H-3,5	H-2″,6″	H-3″,5″
5	7.90	7.94	7.78	6.90
6	7.94	7.99	7.91	7.06
7a	7.98	7.85	—[b)]	—[b)]
8	7.15	7.71	7.76	6.93
9	7.16	7.73	7.84	7.05
10[a)]	7.14	7.71	7.82	6.77

a) Measurement solvent: CD$_2$Cl$_2$. b) The broadened signal, which could not be assigned, was observed (see Figure 2).

Reductions of 5–7a with NaBH$_4$ and Comparative Studies of ^{1}H and ^{13}C NMR Spectral Parameters of 5–10. The reduction of **5** with NaBH$_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 85% yield of **8** (Scheme 2 and Table 6). Compound **8** was obtained as a green powder. A comparative study of the UV–vis spectrum of

Table 4. Selected ^{13}C NMR Chemical Shifts (δ) for the 3-Guaiazulenylmethylium Ions of **5**–**7a** and the 3-Guaiazulenylmethyl Groups of **8**–**10** in CD$_3$CN at 25 °C

Compound	HC-α	C-1′	C-2′	C-3′	C-3a′	C-4′	C-5′	C-6′	C-7′	C-8′	C-8a′
5	148.9	146.7	141.1	140.9	153.6	158.0	150.9	145.1	172.1	139.8	161.6
6	149.0	146.7	141.2	141.0	153.7	158.2	151.0	145.1	172.2	139.9	161.7
7a	149.9	147.3	142.0	141.1	154.5	158.9	151.5	145.9	172.5	140.8	162.0
8	37.4[a)]	125.3	141.9	126.1	133.8	146.3	127.1	135.9	140.2	134.4	138.8
9	37.4[a)]	125.3	141.9	126.0	133.8	146.3	127.2	135.9	140.2	134.4	138.8
10[b)]	36.6[a)]	123.9	140.7	124.8	132.7	145.0	125.8	134.4	138.7	133.0	137.5

a) H$_2$C-3′. b) Measurement solvent: CD$_2$Cl$_2$.

Table 5. The ^{13}C NMR Chemical Shifts (δ) for the Azobenzenes of **5**–**10** in CD$_3$CN at 25 °C

Compound	C-1	C-2,6	C-3,5	C-4	C-1″	C-2″,6″	C-3″,5″	C-4″
5	138.0	135.0	124.0	154.8	147.4	126.3	116.9	161.9
6	138.2	135.0	124.0	154.9	147.9	126.1	115.6	164.1
7a	—[b)]	136.9	120.1	—[b)]	—[b)]	—[b)]	—[b)]	—[b)]
8	147.5	130.0	123.3	151.7	147.3	125.5	116.7	160.8
9	147.8	130.0	123.3	151.7	147.6	125.3	115.3	163.1
10[a)]	144.8	128.6	121.7	150.8	143.1	124.3	111.1	152.1

a) Measurement solvent: CD$_2$Cl$_2$. b) The signal was not observed.

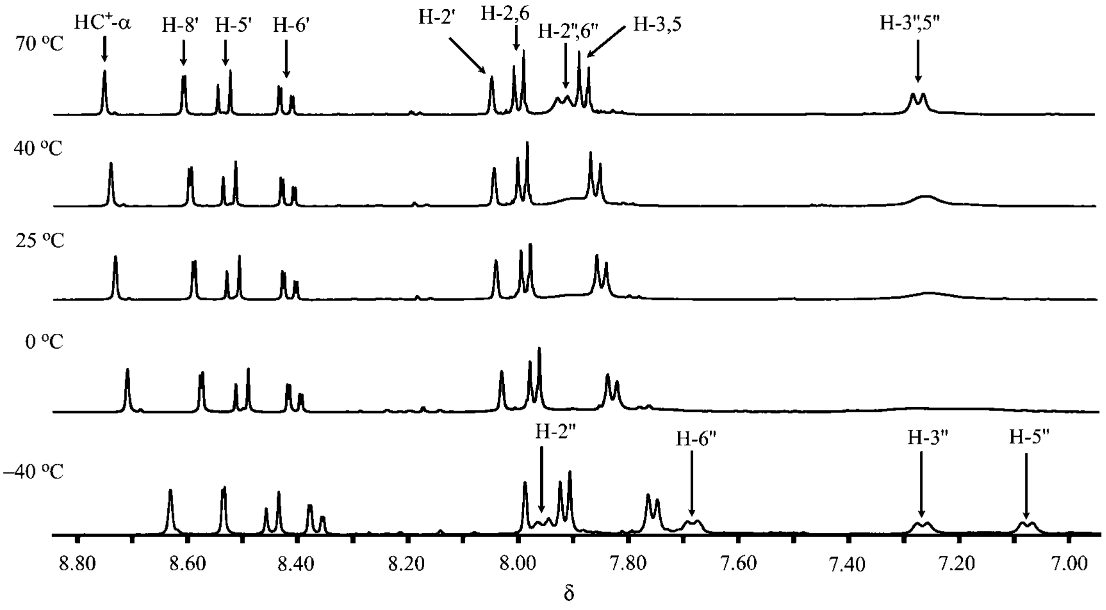


Figure 2. The partial variable-temperature ^{1}H NMR spectra of **7a** in CD_3CN at 70, 40, 25, 0, and −40 °C.

Table 6. The Yield (%) of the Products **8**–**10** Obtained from the Reductions of **5**–**7a** with $NaBH_4$ in a Mixed Solvent of EtOH and CH_3CN at 25 °C for 30 min

Entry	Substituent R	Temp/°C	Time/h	Product	Yield/%[a)]
1	OH	25	30	**8**	85
2	OCH_3	25	30	**9**	74
3	$N(CH_3)_2$	25	30	**10**	72

a) Isolated yield.

Table 7. The Selected UV–Vis and IR Spectral Data of **1** and **5**–**10**

Compound	λ_{max}/nm (log ε)	ν_{max}/cm^{-1} (N=N)
1	244 (4.39), 284 (4.61), 348 (3.65), 600 (2.68)	
5	232 (4.47), 343 (4.29), 498 (4.56)	1601
6	232 (4.50), 346 (4.33), 496 (4.58)	1601
7a	233 (4.42), 414 (4.22), 600 (4.74)	1620
8	246 (4.58), 293 (4.70), 352 (4.56), 620 (2.76)	1593
9	246 (4.57), 293 (4.69), 353 (4.55), 618 (2.74)	1601
10	248 (4.54), 293 (4.71), 413 (4.55), 620 (2.74)	1597

8 with that of **1** (Figure 1b) showed that the characteristic UV–vis absorption bands from **1** were observed (Table 7). The IR spectrum showed specific bands originating from O–H at ν_{max} 3414 cm^{-1}, which was much lower than that of **5** ($\Delta\nu_{max}$ 89 cm^{-1}), and N=N at ν_{max} 1593 cm^{-1}, which was slightly lower than that of **5** ($\Delta\nu_{max}$ 8 cm^{-1}) (Table 7). The molecular formula $C_{28}H_{28}ON_2$ was determined by exact FAB-MS spectrum. The ^{1}H NMR spectrum showed signals from a 3-guaiazulenylmethyl-substituted 4-hydroxyazobenzene at the C-4′ position, the signals of which were carefully assigned using H–H COSY and computer-assisted simulation based on first-order analysis (Tables 2 and 3). The ^{13}C NMR spectrum exhibited 23 carbon signals assigned by HMQC and HMBC (Tables 4 and 5). Thus, the spectroscopic data for **8** led to the molecular structure 4-(3-guaiazulenylmethyl)-4′-hydroxyazobenzene (Scheme 2), in which a hydride-ion attached to the HC^{+}-α carbon atom of **5**, selectively. Comparative studies of the chemical shifts for the ^{1}H and ^{13}C NMR signals of **5** with those of **8** showed that the Me-1′ proton signal for the 3-guaiazulenylmethylium ion of **5** displayed a slight up-field shift in comparison with that of **8**; however, the other proton signals of **5** showed down-field shifts in comparison with those of **8**. The order of larger down-field shift was HC-α ($\Delta\delta$ 4.04) > H-5′ (1.66) > H-6′ (1.07) > Me-4′, H-2′ (0.53, each) > Me_2CH-7′ (0.44) > H-8′ (0.40) > $(CH_3)_2CH$-7′ (0.14). Although the C-2′ and $(CH_3)_2CH$-7′ carbon signals for the 3-guaiazulenylmethylium ion of **5** displayed slight up-field shifts in comparison with those of **8**, the other carbon signals for that of **5** showed down-field shifts in comparison with those of **8**. The order of larger down-field shift was HC-α ($\Delta\delta$ 111.5) > C-7′ (31.9) > C-5′ (23.8) > C-8a′ (22.8) > C-1′ (21.4) > C-3a′ (19.8) > C-3′ (14.8) > C-4′ (11.7) > C-6′ (9.2) > C-8′ (5.4) > Me-4′ (2.9) > Me_2CH-7′ (1.9) > Me-1′ (1.0). The H-2″,6″ and H-3″,5″ proton signals for the 4-hydroxyazobenzene of **5** coincided with those of **8**; however, the other proton signals for **5** were shifted down-field in comparison with those of **8**. The order of larger down-field shift was H-2,6 ($\Delta\delta$ 0.75) > H-3,5 (0.23) > HO-4″ (0.12). Although the C-1, C-2,6, C-3,5, and C-4 carbon signals for the 4-hydroxyazobenzene of **5** revealed up- and down-field shifts in comparison with those of **8**, the C-1″ and C-3″,5″ carbon signals for that of **5** coincided with those of **8** and the C-2″,6″ and C-4″ carbon signals for that of **5** showed slight down field shifts in comparison with those of **8**. Comparing the ^{1}H and ^{13}C NMR chemical shifts of **5** to those of **8**, the resonance structures of **5** can be inferred as illustrated in Chart 2.

The $NaBH_4$-reduction of **6** under the same reaction conditions as for **5** afforded as high as 74% yield of **9** (Scheme 2 and Table 6). Compound **9** was obtained as green blocks. A comparative study on the UV–vis spectrum of **9** with that of **1** (Figure 1b) showed the characteristic UV–vis absorption bands from **1** (Table 7). The IR spectrum showed a specific band originating from N=N at ν_{max} 1601 cm^{-1}, which coincided with that of **6** (Table 7). The molecular formula $C_{29}H_{30}ON_2$ was determined by exact FAB-MS spectrum. The ^1H NMR spectrum showed signals from a 3-guaiazulenylmethyl-substituted 4-methoxyazobenzene at the C-4′ position, the signals of which were carefully assigned using similar techniques to those of **8** (Tables 2 and 3). The ^{13}C NMR spectrum exhibited 24 carbon signals assigned by HMQC and HMBC (Tables 4 and 5). Thus, the spectroscopic data for **9** led to the molecular structure 4-(3-guaiazulenylmethyl)-4′-methoxyazobenzene (Scheme 2), in which a hydride-ion also attached to the HC^+-α carbon atom of **6**, selectively. Comparative studies of the chemical shifts of the ^1H and ^{13}C NMR signals of **6** with those of **9** showed that the Me-1′ proton signal for the 3-guaiazulenylmethylium ion of **6** shifted slightly up-field in comparison with that of **9**; however, the other proton signals for **6** showed down-field shifts in comparison with those of **9**. The order of larger down-field shift was HC-α ($\Delta\delta$ 4.08) > H-5′ (1.68) > H-6′ (1.09) > H-2′ (0.56) > Me-4′ (0.54) > Me_2CH-7′ (0.45) > H-8′ (0.43) > $(CH_3)_2CH$-7′ (0.14). Although the C-2′ and $(CH_3)_2CH$-7′ carbon signals for the 3-guaiazulenylmethylium ion of **6** displayed slight up-field shifts in comparison with **9**, the other carbon signals for **6** showed down-field shifts in comparison with those of **9**. The order of larger down-field shift was HC-α ($\Delta\delta$ 111.6) > C-7′ (32.0) > C-5′ (23.8) > C-8a′ (22.9) > C-1′ (21.4) > C-3a′ (19.9) > C-3′ (15.0) > C-4′ (11.9) > C-6′ (9.2) > C-8′ (5.5) > Me-4′ (2.9) > Me_2CH-7′ (2.0) > Me-1′ (1.0). The H-2″,6″, H-3″,5″, and MeO-4″ proton signals for the 4-methoxyazobenzene of **6** coincided with those of **9**, while the other proton signals for **6** shifted down-field in comparison with those of **9**. The order of larger down-field shift was H-2,6 ($\Delta\delta$ 0.78) > H-3,5 (0.26). The C-1″, C-3″,5″, and MeO-4″ carbon signals for the 4-methoxyazobenzene of **6** coincided with those of **9**; however, the C-1 carbon signal for **6** displayed an up-field shift in comparison with that of **9** and the other carbon signals of **6** showed down-field shifts in comparison with those of **9**. The order of larger down-field shift was C-2,6 ($\Delta\delta$ 5.0) > C-4 (3.2) > C-4″ (1.0) > C-2″,6″ (0.8) > C-3,5 (0.7). Similar to the case of **5**, comparing the ^1H and ^{13}C NMR chemical shifts of **6** to those of **9**, the resonance structures of **6** can be inferred as illustrated in Chart 2.

The $NaBH_4$-reduction of **7a** under the same reaction conditions as for **5** gave as high as 72% yield of **10** (Scheme 2 and Table 6). Compound **10** was obtained as green blocks. A comparative study of the UV–vis spectrum of **10** with that of **1** (Figure 1b) showed characteristic UV–vis absorption bands of **1** (Table 7). The IR spectrum showed a specific band from N=N at ν_{max} 1597 cm^{-1}, which was lower than that of **7a** ($\Delta\nu_{max}$ 23 cm^{-1}), however coincided with those of **8** and **9** (Table 7). The molecular formula $C_{30}H_{33}N_3$ was determined by exact FAB-MS spectrum. The ^1H NMR spectrum showed signals from a 3-guaiazulenylmethyl-substituted 4-(dimethylamino)azobenzene at the C-4′ position, the signals of which were carefully assigned using similar techniques to those of **8** (Tables 2 and 3). The ^{13}C NMR spectrum exhibited 24 carbon signals assigned by HMQC and HMBC techniques (Tables 4 and 5). Thus, the spectroscopic data for **10** led to the molecular structure 4′-(dimethylamino)-4-(3-guaiazulenylmethyl)azobenzene, in which a hydride-ion also attached to the HC^+-α carbon atom of **7a**, selectively. Comparative studies of the chemical shifts for the ^1H and ^{13}C NMR signals of **7a** with those of **10** showed broadening H-2″,6″ and H-3″,5″ proton signals of **7a** which could not be unambiguously assigned, and the C-1, C-4, C-1″, C-2″,6″, C-3″,5″, and C-4″ carbon signals of **7a** were not observed, suggesting the existence of rotational stereoisomers for **7a″** (Chart 2); however, the corresponding signals of **10** were observed. The Me-1′ proton signal for the 3-guaiazulenylmethylium ion of **7a** revealed a slight up-field shift in comparison with that of **10**; however, the other proton signals for **7a** showed down-field shifts in comparison with those of **10**. The order of larger down-field shift was HC-α ($\Delta\delta$ 4.06) > H-5′ (1.69) > H-6′ (1.13) > H-2′ (0.61) > Me-4′ (0.52) > H-8′ (0.48) > Me_2CH-7′ (0.46) > $(CH_3)_2CH$-7′ (0.10). All the carbon signals for the 3-guaiazulenylmethylium ion of **7a** were shifted down-field in comparison with those of **10**. The order of larger down-field shift was HC-α ($\Delta\delta$ 113.3) > C-7′ (33.8) > C-5′ (25.7) > C-8a′ (24.5) > C-1′ (23.4) > C-3a′ (21.8) > C-3′ (16.3) > C-4′ (13.9) > C-6′ (11.5) > C-8′ (7.8) > Me-4′ (4.6) > Me_2CH-7′ (3.9) > Me-1′ (2.6) > C-2′ (1.3) > $(CH_3)_2CH$-7′ (0.8). The observed proton signals for the 4-(dimethylamino)azobenzene of **7a** showed down-field shifts relative to those of **10**. The order of larger down-field shift was H-2,6 ($\Delta\delta$ 0.84) > Me_2N-4″ (0.41) > H-3,5 (0.14). Although the C-3,5 carbon signal for the 4-(dimethylamino)azobenzene of **7a** was up-field compared to that of **10**, the other observed carbon signals for **7a** showed down-field shifts in comparison with those of **10**. The order of larger down-field shift was C-2,6 ($\Delta\delta$ 8.3) > Me_2N-4″ (4.6). From the variable-temperature ^1H NMR spectral data of **7a** and comparative studies of the ^1H and ^{13}C NMR chemical shifts of **7a** with those of **5**, **6**, and **10** (Tables 2–5), the resonance structures of **7a** can be inferred as illustrated in Chart 2.

X-ray Crystal Structure of 7b. Although it was very difficult to obtain a single crystal of **5**–**7a** suitable for X-ray crystallographic analysis, recrystallization of the monocarbenium tetrafluoroborate **7b** from a mixed solvent of acetonitrile and diethyl ether provided a single crystal suitable for that purpose. Therefore, the crystal structure of **7b** could be determined by means of X-ray diffraction at −75 °C. The ORTEP drawing **7b** possessing an equiv of HBF_4 is shown in Figure 3. Comparing the selected bond lengths of **7b** to those of structurally related known compounds [4-(dimethylamino)-phenyl](3-guaiazulenyl)methylium tetrafluoroborate[5] (**11**), 4-(1-azulenylazo)-1-methylpyridium hexafluorophosphate[35] (**12**), and azobenzene[36–38] (**13**) (Chart 3) are shown in Tables 8 and 9. From dihedral angles between least-squares planes, the plane of the 4-[4-(dimethylamino)phenylazo]phenyl group twisted by 11.6° from that of the 3-guaiazulenylmethylium ion structure, because of the influence of steric hindrance and repulsion between the hydrogen atoms of the C-6 and C-2′ positions, the angle of which was smaller than that of **11** (20.7°). Similarly

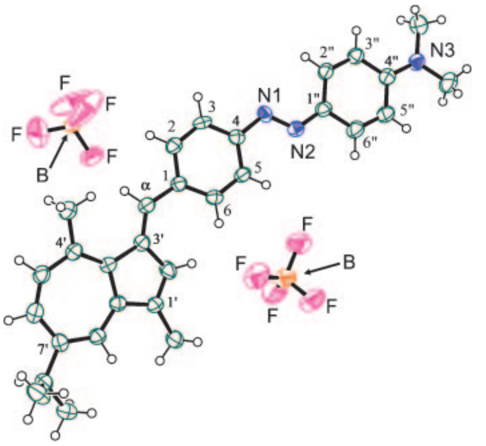


Figure 3. The ORTEP drawing of **7b** with an equiv of HBF$_4$ (see BF$_4$ drawn right) (30% probability thermal ellipsoids). Measurement temperature: −75 °C.

Table 8. The Selected C–C Bond Lengths (Å) for the 3-Guaiazulenylmethylium Ions of **7b** and **11** and the 3-Azulenyl Group of **12**

Atom	**7b**	**11**	**12**[a]
C1′–C2′	1.348(6)	1.351(7)	1.363(11)
C2′–C3′	1.442(6)	1.448(7)	1.424(11)
C3′–C3a′	1.503(6)	1.457(7)	1.425(11)
C3a′–C4′	1.390(6)	1.385(7)	1.384(12)
C4′–C5′	1.407(6)	1.406(7)	1.392(12)
C5′–C6′	1.379(7)	1.373(8)	1.384(12)
C6′–C7′	1.412(6)	1.386(8)	1.382(13)
C7′–C8′	1.382(6)	1.379(8)	1.391(13)
C8′–C8a′	1.399(6)	1.392(7)	1.392(11)
C8a′–C1′	1.446(6)	1.416(7)	1.423(12)
C3a′–C8a′	1.445(6)	1.465(7)	1.455(12)
C3′–Cα	1.360(6)	1.396(7)	—

a) For a comparative purpose, the numbering scheme of the 1-azulenyl group of **12** was changed to that of the 3-azulenyl group (see Chart 3).

Table 9. The Selected Bond Lengths (Å) for the 4-(Dimethylamino)phenyl Groups of **7b** and **11** and the Azobenzenes of **7b** and **13**

Atom	**7b**	**11**	**13**
Cα–C1	1.439(6)	1.414(7)	—
C1–C2	1.405(6)	—	1.382(3)
C2–C3	1.377(6)	—	1.384(3)
C3–C4	1.393(6)	—	1.387(2)
C4–C5	1.403(6)	—	1.389(2)
C5–C6	1.375(6)	—	1.384(3)
C6–C1	1.405(6)	—	1.391(2)
C4–N1	1.400(5)	—	1.428(2)
N1–N2	1.299(5)	—	1.247(2)
N2–C1″	1.324(6)	—	—
C1″–C2″	1.423(6)	1.405(7)[a]	—
C2″–C3″	1.335(6)	1.372(8)[b]	—
C3″–C4″	1.446(6)	1.390(8)[c]	—
C4″–C5″	1.431(7)	1.403(8)[d]	—
C5″–C6″	1.349(7)	1.360(7)[e]	—
C6″–C1″	1.438(6)	1.404(8)[f]	—
C4″–N3	1.341(6)	1.359(7)[g]	—

a) C1–C2. b) C2–C3. c) C3–C4. d) C4–C5. e) C5–C6. f) C6–C1. g) C4–N.

to the case of **11**, the 3-guaiazulenylmethylium ion clearly underwent bond alternation between single and double bonds, suggesting a similar resonance structure to **7a′** (Chart 2). The 4-[4-(dimethylamino)phenylazo]phenyl group also clearly underwent bond alternation between the single and double bonds, suggesting a similar resonance structure to **7a″** (Chart 2). The average C–C bond length of the seven-membered ring of the 3-guaiazulenyl group (1.402 Å) coincided with those of **11** (1.399 Å) and **12** (1.398 Å), the bond length of which was shorter than that of the parent azulene (1.412 Å),[39] and was longer than that of the azulenium ion structure (1.38 Å).[40,41] The C–C bond length of the five-membered ring of the 3-guaiazulenyl group appreciably varied between 1.348 and 1.503 Å; in particular, the C1′–C2′ bond length (1.348 Å) was characteristically shorter than the average C–C bond length for the five-membered ring (1.436 Å), which coincided with the C–C bond lengths observed for the five-membered rings of **11** and **12**. The C3′–Cα bond length (1.360 Å) was also characteristically shorter than the C1–Cα bond length (1.439 Å). The N=N bond length (1.299 Å) coincided with that of **12** (1.295 Å); however, the bond length was longer than that of **13** (1.247 Å). The C4″–N3 bond length (1.341 Å) was shorter than the C4–N bond length of **11** (1.359 Å). The N2–C1″ (1.324 Å), C2″–C3″ (1.335 Å), C5″–C6″ (1.349 Å), and C4″–N3 (1.341 Å) bond lengths were shorter than the Cα–C1 (1.439 Å), C2–C3 (1.377 Å), C5–C6 (1.375 Å), and C4–N1 (1.400 Å) bond lengths. The C4–N1 (1.400 Å) bond length was shorter than that of **13** (1.428 Å). In conclusion, it can be inferred that the C–C and C–N bond lengths based on the X-ray crystallographic analysis of **7b**, compared with those of **11**–**13**, lead to a crystal structure with similar resonance structures to those of **7a** illustrated in Chart 2. From the viewpoint of structural organic chemistry, it is noteworthy that the crystal structure determination of **16**, with an equiv of HPF$_6$, has not yet been achieved; however, the crystal structure of **7b**, with an equiv of HBF$_4$, has been determined.

Electrochemical Behavior of 5–7a. We have been interested further in comparison of the electrochemical properties of the monocarbenium ion compounds **5**–**7a**. The electrochemical behavior of **5**–**7a** was, therefore, measured by means of CV and DPV [Potential (in volt) vs. SCE] in CH$_3$CN containing 0.1 M [n-Bu$_4$N]PF$_6$ as a supporting electrolyte. As a result, it was found that **5** and **6** underwent one-electron reduction at a potential of −0.15 V (E_p) by DPV [−0.21 V (E_pc, irreversible) by CV] for **5** and that of −0.06 V (E_p) by DPV [−0.11 V (E_pc, irreversible) by CV] for **6**, presumably generating the corresponding electrochemically unstable radical species (HC$^\bullet$-1), i.e., (3-guaiazulenyl)[4-(4-hydroxyphenylazo)phenyl]methyl and (3-guaiazulenyl)[4-(4-methoxyphenylazo)phenyl]methyl radical species. Therefore, **6** is slightly more susceptible to reduction than **5**. Interestingly, three reduction potentials observed by DPV were positioned at the E_p values of 0.02, −0.13, and −0.40 V for **7a** and the corresponding three irreversible reduction potentials determined by CV were located at the values of −0.04, −0.18, and −0.45 V (E_pc

each) as shown in Figure 4. Thus, an apparent difference between the electrochemical behavior of **7a** with rotational stereoisomers of **7a″** and that of **5** and **6** without rotational stereoisomers of **5″** and **6″** was observed (Chart 2). The reduction potentials of **7a** coincided with those of (2*E*)-1-azulenyl-3-phenyl-2-propenylium hexafluorophosphate (**14**) [−0.01 V (E_p) by DPV and −0.08 V (E_{pc}) by CV][15] (Chart 4), **5**, (2*E*)-1-(3-guaiazulenyl)-3-phenyl-2-propenylium hexafluorophosphate (**15**) [−0.16 V (E_p) by DPV and −0.23 V (E_{pc}) by CV][15] (Chart 4), **17** [−0.19 V (E_p) by DPV and −0.25 V (E_{pc}) by CV],[20] **11** [−0.39 V (E_p) by DPV and −0.47 V (E_{pc}) by CV],[5] and **18** [−0.43 V (E_p) by DPV and −0.49 V (E_{pc}) by CV][20] (Table 10). From the ^{1}H and ^{13}C NMR spectral parameters, it can be inferred that the positive charges of **14**, **5**, **15**, **17**, **11**, and **18** are mainly localized at the seven-membered ring for **14**, the HC-*α* and HC-1 carbon atoms for **5**, **15**, and **17**, and the nitrogen atoms of the dimethylamino and amino groups for **11** and **18**, forming a 1-azulenylium ion structure, a 3-guaiazulenylmethylium ion structure, and a *p*-benzoquinodimethane monoiminium ion structure, respectively, and further that the three reduction potentials of **7a** are observed owing to the formation of the resonance structures **7a′** and **7a″** with rotational stereoisomers (Chart 2). A plausible electron-transfer mechanism of **7a** derived from the CV and DPV data are noteworthy, and is currently under intensive investigation.

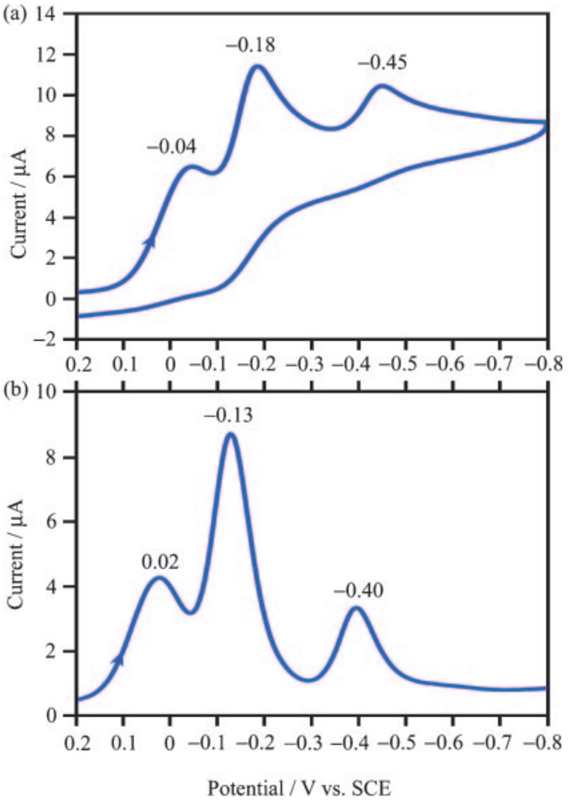
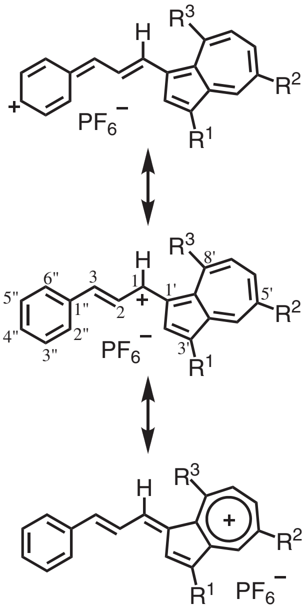


Figure 4. The cyclic (a) and differential pulse (b) voltammograms of **7a** (3.0 mg, 5.2 μmol) in 0.1 M [*n*-Bu$_4$N]PF$_6$, CH$_3$CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (E_p) by DPV and +0.40 V ($E_{1/2}$) by CV under the same electrochemical measurement conditions as for **7a**.

Conclusion

We have reported the following five interesting points in this paper: namely, (i) the reaction of guaiazulene (**1**) with 4′-hydroxyazobenzene-4-carbaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave as high as 94% yield of the target monocarbenium ion compound (3-guaiazulenyl)[4-(4-hydroxyphenylazo)phenyl]methylium hexafluorophosphate (**5**). Similarly, the reactions of **1** with 4′-methoxyazobenzene-4-carbaldehyde (**3**) and 4′-(dimethylamino)azobenzene-4-carbaldehyde (**4**) under the same reaction conditions as for **2** afforded the corresponding monocarbenium ion compounds (3-guaiazulenyl)[4-(4-methoxyphenylazo)phenyl]methylium hexafluorophosphate (**6**) and {4-[4-(dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium hexafluorophosphate (**7a**) in 97 and 95%



14: R^1 = R^2 = R^3 = H
15: R^1 = R^3 = CH$_3$, R^2 = CH(CH$_3$)$_2$

Chart 4.

Table 10. The Reduction Potential(s) (E_{pc}/V) of **5**–**7a**, **11**, **14**, **15**, **17**, and **18** by Means of CV under the Same Electrochemical Measurement Conditions as for **7a**

Compound	5	6	7a	11	14	15	17	18
E^1_{red}/V	−0.21	−0.11	−0.04	−0.47	−0.08	−0.23	−0.25	−0.49
E^2_{red}/V			−0.18					
E^3_{red}/V			−0.45					

yields; (ii) the reduction of **5** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 85% yield of 4-(3-guaiazulenylmethyl)-4′-hydroxyazobenzene (**8**), in which a hydride-ion attached to the HC^+-α carbon atom of **5**, selectively. Similarly, the $NaBH_4$-reductions of **6** and **7a** under the same reaction conditions as for **5** afforded the corresponding hydride-reduction products 4-(3-guaiazulenylmethyl)-4′-methoxyazobenzene (**9**) and 4′-dimethylamino-4-(3-guaiazulenylmethyl)azobenzene (**10**) in 74 and 72% yields; (iii) along with comparative studies of the ^{1}H and ^{13}C NMR chemical shifts of **5**–**7a** with those of **8**–**10**, apparently indicating the difference between the delocalized π-electron system of **7a** and those of **5** and **6** owing to the influence of the substituted HO–, CH_3O–, or $(CH_3)_2N$– group at the C4″ position, the variable-temperature ^{1}H NMR studies of **7a** in acetonitrile-d_3 at 70, 40, 25, 0, and −40 °C, supporting the formation of rotational stereoisomers for **7a″**, were reported; (iv) although X-ray crystallographic analysis of **5**–**7a** has not yet been achieved because of difficulty in obtaining a single crystal suitable for that purpose, the crystal structure of {4-[4-(dimethylamino)phenylazo]phenyl}(3-guaiazulenyl)methylium tetrafluoroborate (**7b**) with an equiv of HBF_4 was determined by X-ray diffraction at −75 °C, supporting the formation of **7b**, with similar resonance structures to those of **7a**, in the single crystal; and (v) an apparent difference between the electrochemical behavior of **7a** and that of **5** and **6** was observed.

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