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Preparation and Structures of New Azobenzene Derivatives with a 3-Guaiazulenylvinyl Group

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Wittig reactions of (*E*)-4-(4-methoxyphenyldiazenyl)benzaldehyde and (*E*)-4-[4-(dimethylamino)phenyldiazenyl]-benzaldehyde with (3-guaiazulenylmethyl)triphenylphosphonium bromide in ethanol in the presence of sodium ethoxide at 25 °C for 24 h under argon give only E forms (*E*)-4-{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}methoxybenzene and (*E*)-*N*,*N*-dimethyl-4-{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}aniline in 71 and 73% yields. Comparative studies on spectroscopic properties and crystal structures of the two new extended π-electron systems with those of structurally related (and delocalized) π-electron systems (3-guaiazulenyl)[(*E*)-4-(4-methoxyphenyldiazenyl)phenyl]methylium ion and {(*E*)-4-[4-(dimethylamino)phenyldiazenyl]phenyl}(3-guaiazulenyl)methylium ion compounds are reported. Similarly, Wittig reaction of (*E*)-diphenyldiazene-4,4′-dicarbaldehyde with the same reagent under the same reaction conditions as the above affords only E forms (*E*)-4-{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}benzaldehyde and (*E*)-bis{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyl}diazene in 7 and 24% yields. Furthermore, reaction of guaiazulene (=7-isopropyl-1,4-dimethylazulene) with (*E*)-diphenyldiazene-4,4′-dicarbaldehyde in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min provides (*E*)-diphenyldiazene-4,4′-bis(3-guaiazulenylmethylium) bis(hexafluorophosphate) in 46% yield which upon reduction with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gives (*E*)-bis[4-(3-guaiazulenylmethyl)phenyl]diazene in 88% yield. Comparative studies of spectroscopic properties of a new extended π-electron system (*E*)-bis{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyl}diazene with those of a new delocalized π-electron system (*E*)-diphenyldiazene-4,4′-bis(3-guaiazulenylmethylium) bis(hexafluorophosphate) are documented.

In previous papers,[1–20] we reported facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of new conjugated π-electron systems possessing a 3-guaiazulenyl (=5-isopropyl-3,8-dimethylazulen-1-yl)[1–16,18–20] [or an azulen-1-yl[8,15] or a 3-(methoxycarbonyl)azulen-1-yl[17]] group. During the course of our basic and systematic investigations of azulenes, we quite recently found the following interesting results.[21] Namely, the reaction of naturally occurring guaiazulene[22] (**9**) with (*E*)-4-(4-hydroxyphenyldiazenyl)benzaldehyde in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave as high as 94% yield of **12** (Chart 1). Similarly, reactions of **9** with diazenes **2** and **3** under the same reaction conditions as the above afforded **13** and **14a** (Chart 1) in 97 and 95% yields. Reduction of **12** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 85% yield of **15**, in which a hydride ion attached to the HC^+-α carbon atom of **12**, selectively (Scheme 1). Similarly, $NaBH_4$-reductions of **13** and **14a** under the same reaction conditions as for **12** afforded **16** and **17** in 74 and 72% yields (Scheme 1). Along with comparative studies of the ^1H and ^{13}C NMR chemical shifts of the delocalized π-electron systems of **12**–**14a** with those of the hydride reduction products **15**–**17**, apparently indicating the difference between the delocalized π-electron system of **14a** and those of **12** and **13** owing to the influence of the substituted $(CH_3)_2N$–, HO–, or CH_3O– group at the C4″ position of azobenzene, the variable-temperature ^1H NMR studies of **14a** in acetonitrile-d_3 at 70, 40, 25, 0, and −40 °C, supporting the formation of rotational stereoisomers of **14a″** (Chart 1) were reported. Although X-ray crystallographic analysis of **12**–**14a** has not yet been achieved because of difficulty in obtaining a single crystal suitable for that purpose, the crystal structure of **14b** with an equiv of HBF_4 (Chart 2) could be determined by means of X-ray diffraction at −75 °C, supporting the formation of **14b**, with similar resonance structures to those of **14a**, in the single crystal.

Moreover, our interest has quite recently been focused on the structures and the spectroscopic properties of the three new extended π-electron systems **4**, **5**, and **8** (Chart 3) compared with those of structurally related (and delocalized) π-electron systems **13**, **14a**, and **10** (Chart 4). In relation to extended π-electron systems with an azulenyl group, for example, styrylazulenes (=1-azulenyl-2-phenylethylenes) were prepared by Wittig reactions of azulenecarbaldehydes with benzyltriphenylphosphonium chloride and further, the reverse Wittig reaction [i.e., the reaction of benzaldehyde with (azulenylmethyl)triphenylphosphonium iodide] was applied to the preparation of styrylazulenes.[23,24] On the other hand, azobenzenes in general are currently drawing increasing interest from the viewpoint of potential utilities as photomemories,[25,26] optical switching,[27–29] and optoelectronics.[30,31]

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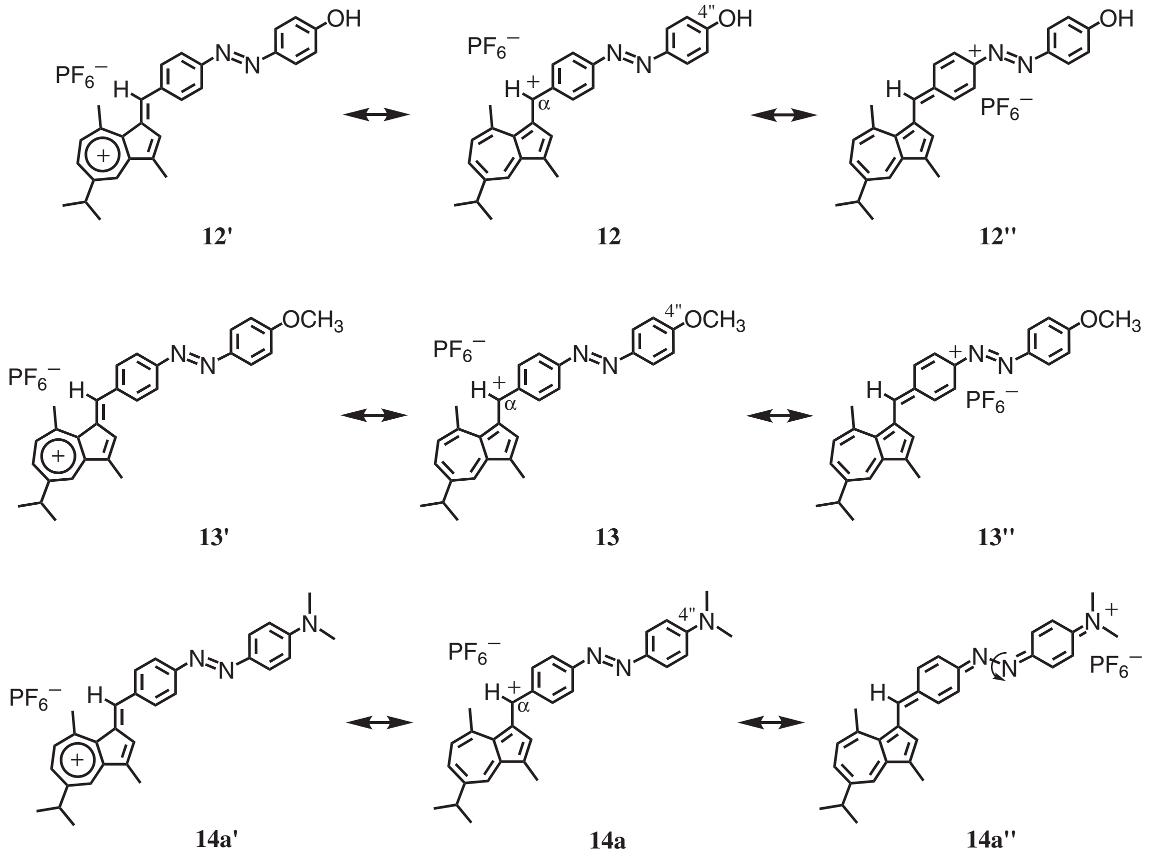
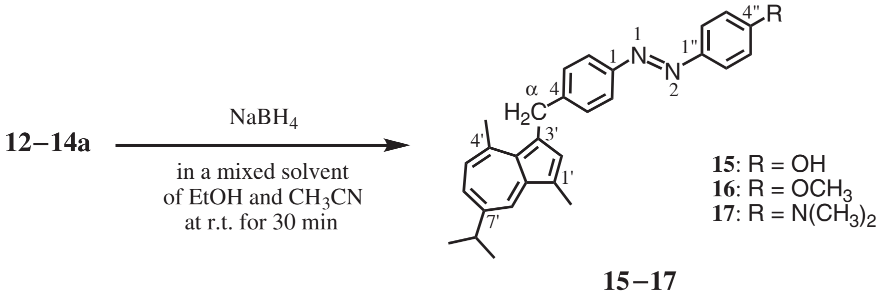


Chart 1.



Scheme 1. The reductions of **12**–**14a** with $NaBH_4$ in a mixed solvent of EtOH and CH_3CN at 25 °C for 30 min, affording the corresponding hydride-reduction products **15**–**17**.

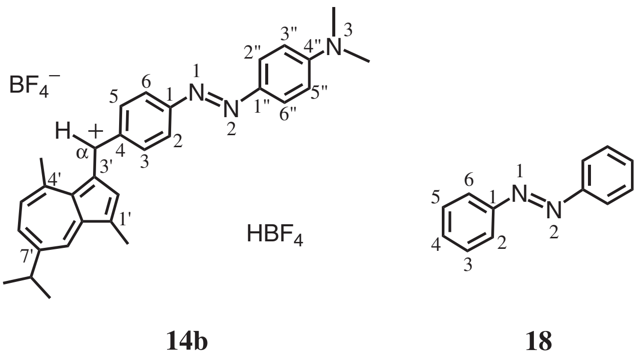
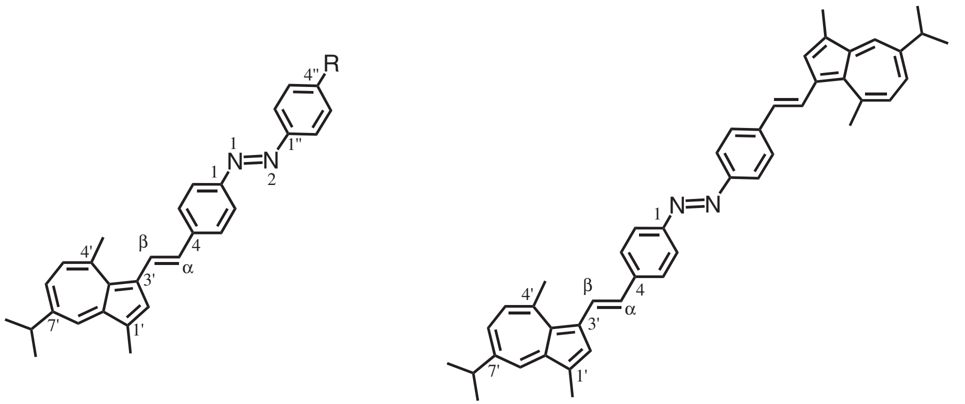


Chart 2. For comparative purposes, the numbering scheme of **14b** was changed.

We now wish to report the following five interesting points for the title studies: namely, (i) preparation and spectroscopic properties of **4** and **5**; (ii) ^{1}H and ^{13}C NMR spectral parameters of **13** (and **14a**) compared with those of **4** (and **5**); (iii) crystal structures of **4** and **5** compared with that of **14b** (Chart 2); (iv) preparation and spectroscopic properties of **8** and **10** which upon reduction with $NaBH_4$ gives **11** (Chart 4); and (v) ^{1}H and ^{13}C NMR spectral parameters of **10** compared with those of **11** (and **8**).

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. FAB-MS spectra were taken on a JEOL Tandem MStation JMS-700 TKM data system. UV–vis and IR

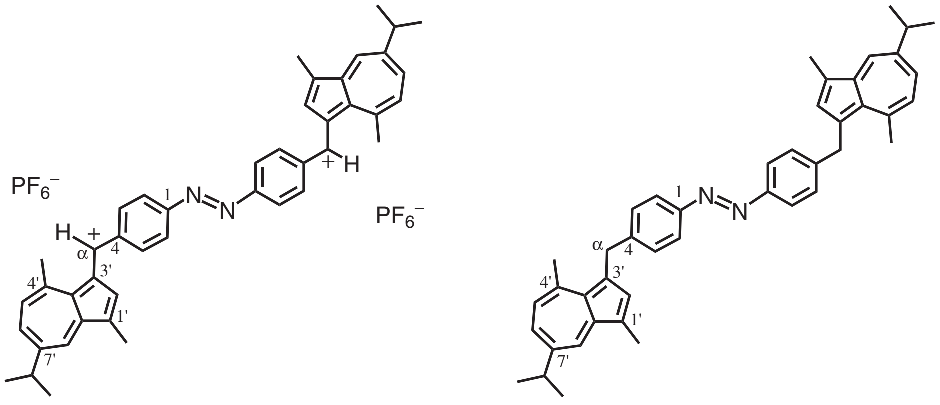


4, **5**, and **7**

8

4: R = OCH_3, **5**: R = $N(CH_3)_2$, **7**: R = CHO

Chart 3. For comparative purposes for ^{1}H and ^{13}C NMR signals and crystal structures, the numbering schemes of compounds **4**, **5**, and **7** were changed.



10

11

Chart 4.

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), JEOL JNM-ECA600 (600 MHz for ^{1}H and 150 MHz for ^{13}C), and JNM-ECA700 (700 MHz for ^{1}H and 176 MHz for ^{13}C) cryospectrometer at 25 °C. The ^{1}H NMR spectra (δ and J values) were assigned 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.

Preparation of (*E*)-4-{(*E*)-4-[2-(3-Guaiazulenyl)vinyl]phenyldiazenyl}methoxybenzene (4). To a solution of (*E*)-4-(4-methoxyphenyldiazenyl)benzaldehyde[21] (**2**) (50 mg, 208 µmol) in ethanol (2 mL) was added a solution of 3-(guaiazulenylmethyl)-triphenylphosphonium bromide[32] (**1**) (117 mg, 211 µmol) in ethanol (2 mL) containing sodium ethoxide (15 mg, 221 µmol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture, and then the resulting product was extracted with dichloromethane (20 mL × 3). The extract was washed with distilled water, dried (Na_2SO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with dichloromethane as an eluant. The crude product was recrystallized from dichloromethane–methanol (1:4, v/v) (several times) to provide pure **4** as stable crystals (65 mg, 149 µmol, 71% yield).

Compound **4**: Dark green plates, mp 172 °C [determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]; $R_f = 0.38$ on silica gel TLC (solv. hexane–EtOAc = 8:2, v/v); UV–vis $\lambda_{\max}$/nm (log ε) in CH_2Cl_2: 238 (4.45), 276 (4.43), 359 (4.44), and 481 (4.66); IR $\nu_{\max}$/cm^{-1} (KBr): 1582 (N=N); exact EI-MS (70 eV), found: m/z 434.2336 (M$^+$, 100%); calcd for $C_{30}H_{30}ON_2$: M$^+$, m/z 434.2358; 700 MHz ^{1}H NMR (CD_2Cl_2): signals resulting from the 3-guaiazulenylvinyl group: δ 1.34 (6H, d, $J = 7.0$ Hz, $(CH_3)_2$CH-7′), 2.62 (3H, s, Me-1′), 3.02 (1H, sept, $J = 7.0$ Hz, Me$_2$C*H*-7′), 3.08 (3H, s, Me-4′), 6.92 (1H, d, $J = 10.5$ Hz, H-5′), 7.01 (1H, d, $J = 15.8$ Hz, H-α), 7.28 (1H, dd, $J = 10.5, 2.0$ Hz, H-6′), 7.97 (1H, s, H-2′), 8.03 (1H, d, $J = 2.0$ Hz, H-8′), and 8.17 (1H, d, $J = 15.8$ Hz, H-β); signals originating from 4-methoxyazobenzene: δ 3.89 (3H, s, MeO-4″), 7.03 (2H, ddd, $J = 9.0, 3.1, 2.0$ Hz, H-3″,5″), 7.63 (2H, ddd, $J = 8.4, 2.2, 1.7$ Hz, H-3,5), 7.88 (2H, ddd, $J = 8.4, 2.2, 1.7$ Hz, H-2,6), and 7.92 (2H, ddd, $J = 9.0, 3.1, 2.0$ Hz, H-2″,6″); 176 MHz ^{13}C NMR (CD_2Cl_2): δ 161.7 (C-4″), 150.8 (C-1), 146.9 (C-1″), 145.8 (C-4′), 141.5 (C-7′), 141.0 (C-4), 140.7 (C-8a′), 135.0 (C-6′), 134.7 (C-2′), 133.5 (C-8′), 132.8 (C-3a′), 127.6 (C-5′), 127.1 (C-β), 126.3 (C-1′), 126.0 (C-3,5), 125.5 (C-3′), 124.8 (C-α), 124.1 (C-2″,6″), 122.8 (C-2,6), 113.9 (C-3″,5″), 53.2 (MeO-4″), 37.3 (Me$_2$*C*H-7′), 28.1 (Me-4′), 23.8 ((CH_3)$_2$CH-7′), and 12.4 (Me-1′). For comparative purposes on ^{1}H and ^{13}C NMR signals, the numbering scheme of compound **4** was changed as shown in Chart 3.

X-ray Crystal Structure of (*E*)-4-{(*E*)-4-[2-(3-Guaiazulenyl)-vinyl]phenyldiazenyl}methoxybenzene (4). A total 5630 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 (SIR97)[34] and expanded using Fourier techniques (DIRDIF94).[35] 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.[36] Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-669774 for compound No. **4**. 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 **4**: $C_{30}H_{30}ON_2$ (FW: 434.58), dark green plate (the crystal size, 0.30 × 0.30 × 0.30 mm^3), triclinic, $P\bar{1}$ (#2), $a = 13.474(2)$ Å, $b = 15.431(4)$ Å, $c = 5.746(1)$ Å, $\alpha = 95.11(2)°$, $\beta = 95.95(1)°$, $\gamma = 96.31(1)°$, $V = 1174.9(5)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.228$ g cm^{-3}, μ(Mo Kα) = 0.74 cm^{-1}, Scan width: $(1.21 + 0.30 \tan\theta)°$, Scan mode: ω–2θ, Scan rate: 8.0° min^{-1}, measured reflections: 5630, observed reflections: 5399, No. of parameters: 298, $R1 = 0.058$, $wR2 = 0.188$, and Goodness of fit indicator: 1.27.

Preparation of (*E*)-*N*,*N*-Dimethyl-4-{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}aniline (5). To a solution of (*E*)-4-[4-(dimethylamino)phenyldiazenyl]benzaldehyde[21] (**3**) (50 mg, 197 µmol) in ethanol (20 mL) was added a solution of 3-(guaiazulenylmethyl)triphenylphosphonium bromide[32] (**1**) (110 mg, 198 µmol) in ethanol (5 mL) containing sodium ethoxide (15 mg, 221 µmol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture, and then the resulting product was extracted with dichloromethane (20 mL × 3). The extract was washed with distilled water, dried (Na_2SO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with dichloromethane as an eluant. The crude product was recrystallized from dichloromethane–methanol (1:4, v/v) (several times) to provide pure **5** as stable crystals (65 mg, 145 µmol, 73% yield).

Compound **5**: Dark green plates, mp 233 °C [determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]; $R_f = 0.30$ on silica gel TLC (solv. hexane–EtOAc = 8:2, v/v); UV–vis $\lambda_{\max}$/nm (log ε) in CH_2Cl_2: 255 (4.43), 281 (4.43), and 493 (4.79); IR $\nu_{\max}$/cm^{-1} (KBr): 1601 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: *m/z* 447.2663; calcd for $C_{31}H_{33}N_3$: M$^+$, *m/z* 447.2675; 600 MHz ^{1}H NMR (CD_2Cl_2): signals resulting from the 3-guaiazulenylvinyl group: δ 1.34 (6H, d, $J = 7.0$ Hz, (CH_3)$_2$CH-7′), 2.62 (3H, s, Me-1′), 3.02 (1H, sept, $J = 7.0$ Hz, Me$_2$*CH*-7′), 3.08 (3H, s, Me-4′), 6.90 (1H, d, $J = 11.0$ Hz, H-5′), 7.00 (1H, d, $J = 15.8$ Hz, H-α), 7.27 (1H, dd, $J = 11.0$, 2.0 Hz, H-6′), 7.96 (1H, s, H-2′), 8.02 (1H, d, $J = 2.0$ Hz, H-8′), and 8.14 (1H, d, $J = 15.8$ Hz, H-β); signals resulting from 4-(dimethylamino)azobenzene: δ 3.08 (6H, s, Me$_2$N-4″), 6.78 (2H, ddd, $J = 9.0$, 3.1, 2.0 Hz, H-3″,5″), 7.61 (2H, ddd, $J = 8.5$, 2.1, 1.6 Hz, H-3,5), 7.83 (2H, ddd, $J = 8.5$, 2.1, 1.6 Hz, H-2,6), and 7.86 (2H, ddd, $J = 9.0$, 3.1, 2.0 Hz, H-2″,6″); 150 MHz ^{13}C NMR (CD_2Cl_2): δ 152.7 (C-4″), 151.9 (C-1), 146.4 (C-4′), 144.0 (C-1″), 142.0 (C-7′), 141.3 (C-8a′), 140.6 (C-4), 135.7 (C-2′), 135.4 (C-6′), 134.1 (C-8′), 133.3 (C-3a′), 128.1 (C-5′), 127.2 (C-β), 126.9 (C-1′), 126.6 (C-3,5), 126.3 (C-3′), 125.8 (C-α), 125.0 (C-2″,6″), 123.0 (C-2,6), 111.8 (C-3″,5″), 40.4 (Me$_2$N-4″), 38.0 (Me$_2$*C*H-7′), 28.8 (Me-4′), 24.4 ((CH_3)$_2$CH-7′), and 13.1 (Me-1′). For comparative purposes on ^{1}H and ^{13}C NMR signals, the numbering scheme of compound **5** was changed as shown in Chart 3.

X-ray Crystal Structure of (*E*)-*N*,*N*-Dimethyl-4-{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}aniline (5). A total of 3325 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 (SIR97)[34] and expanded using Fourier techniques (DIRDIF94).[35] 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.[36] Deposition number CCDC-669775 for compound No. **5**.

Crystallographic data for **5**: $C_{31}H_{33}N_3$ (FW: 447.62), dark green plate (the crystal size, 0.40 × 0.40 × 0.50 mm^3), monoclinic, $P2_1$ (#4), $a = 13.750(3)$ Å, $b = 5.921(3)$ Å, $c = 16.596(3)$ Å, $\beta = 110.57(1)°$, $V = 1265.0(6)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.175$ g cm^{-3}, μ(Mo Kα) = 0.69 cm^{-1}, Scan width: $(1.31 + 0.30 \tan\theta)°$, Scan mode: ω–2θ, Scan rate: 8.0° min^{-1}, measured reflections: 3325, observed reflections: 3193, No. of parameters: 307, $R1 = 0.064$, $wR2 = 0.210$, and Goodness of fit indicator: 1.78.

Preparation of (*E*)-{(*E*)-4-[2-(3-Guaiazulenyl)vinyl]phenyldiazenyl}benzaldehyde (7) and (*E*)-Bis{(*E*)-4-[2-(3-guaiazulenyl)vinyl]phenyl}diazene (8). To a solution of (*E*)-diphenyldiazene-4,4′-dicarbaldehyde[37] (**6**) (30 mg, 125 µmol) in ethanol (20 mL) was added a solution of 3-(guaiazulenylmethyl)triphenylphosphonium bromide[32] (**1**) (150 mg, 270 µmol) in ethanol (5 mL) containing sodium ethoxide (20 mg, 294 µmol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture, and then the resulting products were extracted with dichloromethane (20 mL × 3). The extract was washed with distilled water, dried (Na_2SO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with dichloromethane–hexane (6:4, v/v) as an eluant. The starting material **6** (3 mg, 12 µmol, 10%) was recovered. The separated crude products **7** and **8** were recrystallized from dichlorometane–methanol (1:4, v/v) (several times), respectively, to provide pure **7** (4 mg, 9 µmol, 7% yield) and **8** (19 mg, 30 µmol, 24% yield).

Compound **7**: Dark green prisms, mp 172 °C [determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]; $R_f = 0.16$ on silica gel TLC (solv. dichloromethane–hexane = 6:4, v/v); UV–vis $\lambda_{\max}$/nm (log ε) in CH_2Cl_2: 253 (4.31), 278 (4.39), 330 (4.38), and 528 (4.49); IR $\nu_{\max}$/cm^{-1} (KBr): 1701 (C=O) and 1585 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: *m/z* 432.2177; calcd for $C_{30}H_{28}ON_2$: M$^+$, *m/z* 432.2203; 700 MHz ^{1}H NMR (CD_2Cl_2): signals resulting from the 3-guaiazulenylvinyl group: δ 1.35 (6H, d, $J = 7.0$ Hz, (CH_3)$_2$CH-7′), 2.62 (3H, s, Me-1′), 3.03 (1H, sept, $J = 7.0$ Hz, Me$_2$*CH*-7′), 3.09 (3H, s, Me-4′), 6.94 (1H, d, $J = 10.5$ Hz, H-5′), 7.03 (1H, d, $J = 15.6$ Hz, H-α), 7.30 (1H, dd, $J = 10.5$, 2.0 Hz, H-6′), 7.98 (1H, s, H-2′), 8.04 (1H, d, $J = 2.0$ Hz, H-8′), and 8.23 (1H, d, $J = 15.6$ Hz, H-β); signals resulting from 4-formylazobenzene: δ 7.66 (2H, ddd, $J = 8.4$, 2.0, 1.7 Hz, H-3,5), 7.97 (2H, ddd, $J = 8.4$, 2.0, 1.7 Hz, H-2,6), 8.02 (2H, ddd, $J = 8.5$, 2.1, 1.1 Hz, H-3″,5″), 8.04 (2H, ddd, $J = 8.5$, 2.1, 1.1 Hz, H-2″,6″), and 10.08 (1H, s, OHC-4″); 176 MHz ^{13}C NMR (CD_2Cl_2): δ 191.1 (OHC-4″), 155.9 (C-1″), 150.7 (C-1), 145.8 (C-4′), 142.7 (C-4), 141.9 (C-7′), 140.9 (C-8a′), 136.9 (C-4″), 134.9 (C-2′), 134.9 (C-6′), 133.6 (C-8′), 133.2 (C-3a′), 130.2 (C-3″,5″), 128.1 (C-5′), 128.0 (C-β), 126.5 (C-1′), 126.0 (C-3,5), 125.4 (C-3′), 124.4 (C-α), 123.6 (C-2,6), 122.8 (C-2″,6″), 37.3 (Me$_2$*C*H-7′), 28.1 (Me-4′), 23.7 ((*C*H$_3$)$_2$CH-7′), and 12.4 (Me-1′). For comparative purposes on ^{1}H and ^{13}C NMR signals, the numbering scheme of compound **7** was changed as shown in Chart 3.

Compound **8**: Dark green powder, mp 263 °C [determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]; $R_f = 0.48$ on silica gel TLC (solv. dichloromethane–hexane = 6:4, v/v); UV–vis λ_{max}/nm (log ε) in CH_2Cl_2: 230 (4.43), 278 (4.50), 312 (4.47), and 533 (4.71); IR ν_{max}/cm^{-1} (KBr): 1585 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 626.3647; calcd for $C_{46}H_{46}N_2$: M$^+$, m/z 626.3661; 500 MHz ^{1}H NMR (CD_2Cl_2): signals resulting from two equivalent 3-guaiazulenylvinyl groups: δ 1.34 (12H, d, $J = 6.9$ Hz, (C*H*$_3$)$_2$CH-7′), 2.62 (6H, s, Me-1′), 3.02 (2H, sept, $J = 6.9$ Hz, Me$_2$C*H*-7′), 3.09 (6H, s, Me-4′), 6.93 (2H, d, $J = 11.0$ Hz, H-5′), 7.03 (2H, d, $J = 15.8$ Hz, H-α), 7.29 (2H, dd, $J = 11.0$, 2.2 Hz, H-6′), 7.98 (2H, s, H-2′), 8.03 (2H, d, $J = 2.2$ Hz, H-8′), and 8.21 (2H, d, $J = 15.8$ Hz, H-β); signals resulting from two equivalent phenyl groups of an azobenzene: δ 7.65 (4H, ddd, $J = 8.5$, 2.1, 1.8 Hz, H-3,5) and 7.92 (4H, ddd, $J = 8.5$, 2.1, 1.8 Hz, H-2,6); 125 MHz ^{13}C NMR (CD_2Cl_2): δ 151.0 (C-1), 145.8 (C-4′), 141.6 (C-7′), 141.3 (C-4), 140.8 (C-8a′), 135.0 (C-2′), 134.8 (C-6′), 133.6 (C-8′), 132.9 (C-3a′), 127.7 (C-5′), 127.3 (C-β), 126.4 (C-1′), 126.0 (C-3,5), 125.6 (C-3′), 124.8 (C-α), 123.0 (C-2,6), 37.4 (Me$_2$*C*H-7′), 28.2 (Me-4′), 23.8 ((*C*H$_3$)$_2$CH-7′), and 12.4 (Me-1′).

Preparation of (*E*)-Diphenyldiazene-4,4′-bis(3-guaiazulenylmethylium) Bis(hexafluorophosphate) (10). To a solution of commercially available guaiazulene (**9**) (50 mg, 252 µmol) in methanol (1.0 mL) was added a solution of (*E*)-diphenyldiazene-4,4′-dicarbaldehyde[37] (**6**) (30 mg, 125 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-red solid of **10**, 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 (1:5, v/v) (several times) to provide pure **10** as stable crystals (52 mg, 58 µmol, 46% yield).

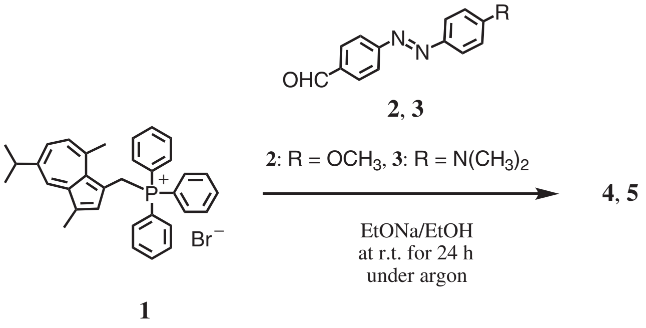
Compound **10**: Dark red prisms, mp >178 °C [decomp., determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]. Found: C, 57.46; H, 4.81; N, 3.28%. Calcd for $2C_{44}H_{44}N_2F_{12}P_2 + 3H_2O$: C, 57.58; H, 5.16; N, 3.05%; UV–vis λ_{max}/nm (log ε) in CH_3CN: 233 (4.76), 288 (4.52), 334 (4.46), 390sh (4.45), and 499 (4.86); IR ν_{max}/cm^{-1} (KBr): 1601 (N=N) and 837, 556 (PF_6^-); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 600.3509; calcd for $C_{44}H_{44}N_2$: [M − 2PF$_6$]$^{2+}$, m/z 600.3505; 500 MHz ^{1}H NMR (CD_3CN): signals resulting from two equivalent 3-guaiazulenylmethylium substituents: δ 1.46 (12H, d, $J = 7.0$ Hz, (C*H*$_3$)$_2$CH-7′), 2.53 (6H, s, Me-1′), 3.39 (6H, s, Me-4′), 3.51 (2H, sept, $J = 7.0$ Hz, Me$_2$C*H*-7′), 8.02 (2H, s, H-2′), 8.45 (2H, dd, $J = 11.2$, 2.2 Hz, H-6′), 8.58 (2H, d, $J = 11.2$ Hz, H-5′), 8.60 (2H, d, $J = 2.2$ Hz, H-8′), and 8.80 (2H, s, HC$^+$-α); signals resulting from two equivalent phenyl groups of an azobenzene: δ 8.03 (4H, ddd, $J = 8.3$, 2.0, 1.7 Hz, H-3,5) and 8.15 (4H, ddd, $J = 8.3$, 2.0, 1.7 Hz, H-2,6); 125 MHz ^{13}C NMR (CD_3CN): δ 172.8 (C-7′), 162.0 (C-8a′), 158.4 (C-4′), 154.6 (C-1), 153.7 (C-3a′), 151.4 (C-5′), 148.4 (HC$^+$-α), 147.2 (C-1′), 145.4 (C-6′), 141.7 (C-3′), 141.0 (C-2′), 140.1 (C-8′), 139.7 (C-4), 134.8 (C-3,5), 124.6 (C-2,6), 40.3 (Me$_2$*C*H-7′), 29.7 (Me-4′), 23.7 ((*C*H$_3$)$_2$CH-7′), and 13.9 (Me-1′).

Reduction of (*E*)-Diphenyldiazene-4,4′-bis(3-guaiazulenylmethylium) Bis(hexafluorophosphate) (10) with NaBH$_4$. To a solution of NaBH$_4$ (5 mg, 132 µmol) in ethanol (2.0 mL) was added a solution of **10** (30 mg, 33 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 and 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 (8:2, v/v) as an eluant. The crude product thus obtained was recrystallized from dichloromethane–methanol (1:5, v/v) (several times) to provide pure (*E*)-bis[4-(3-guaiazulenylmethyl)phenyl]diazene (**11**) as stable crystals (18 mg, 29 µmol, 88% yield).

Compound **11**: Dark green prisms, mp 215 °C [determined by thermal analysis (TGA and DTA: rt → 500 °C/5 °C min^{-1})]. $R_f = 0.60$ on silica gel TLC (solv. hexane–EtOAc = 8:2, v/v); IR ν_{max}/cm^{-1} (KBr): 1596 (N=N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: m/z 602.3657; calcd for $C_{44}H_{46}N_2$: M$^+$, m/z 602.3661; 500 MHz ^{1}H NMR (CD_2Cl_2): signals resulting from two equivalent 3-guaiazulenylmethyl groups: δ 1.34 (12H, d, $J = 6.8$ Hz, (C*H*$_3$)$_2$CH-7′), 2.61 (6H, s, Me-1′), 2.82 (6H, s, Me-4′), 3.03 (2H, sept, $J = 6.8$ Hz, Me$_2$C*H*-7′), 4.69 (4H, s, CH$_2$-3′), 6.82 (2H, d, $J = 11.0$ Hz, H-5′), 7.28 (2H, dd, $J = 11.0$, 2.0 Hz, H-6′), 7.40 (2H, s, H-2′), and 8.11 (2H, d, $J = 2.0$ Hz, H-8′); signals resulting from two equivalent phenyl groups of an azobenzene: δ 7.14 (4H, ddd, $J = 8.7$, 2.3, 2.0 Hz, H-3,5) and 8.05 (4H, ddd, $J = 8.7$, 2.3, 2.0 Hz, H-2,6); 125 MHz ^{13}C NMR (CD_2Cl_2): δ 150.8 (C-1), 145.0 (C-4′), 144.9 (C-4), 140.6 (C-2′), 138.9 (C-7′), 137.5 (C-8a′), 134.4 (C-6′), 133.1 (C-8′), 132.7 (C-3a′), 128.2 (C-3,5), 126.0 (C-5′), 125.2 (C-2,6), 124.4 (C-3′), 123.9 (C-1′), 37.3 (Me$_2$*C*H-7′), 36.5 (CH$_2$-3′), 26.1 (Me-4′), 23.9 ((*C*H$_3$)$_2$CH-7′), and 12.2 (Me-1′).

Results and Discussion

Preparation and Spectroscopic Properties of 4 and 5. The target extended π-electron systems **4** and **5** were prepared according to Scheme 2. The structures of the products **4** and **5** were established on the basis of spectroscopic data [UV–vis, IR, exact MS (EI for **4** and FAB for **5**), ^{1}H and ^{13}C NMR including 2D NMR (i.e., H–H COSY, HMQC, and HMBC)].



Scheme 2. The reactions of **1** with **2** (and **3**) in ethanol in the presence of sodium ethoxide at 25 °C for 24 h under argon, affording the corresponding azobenezene derivatives **4** (and **5**).

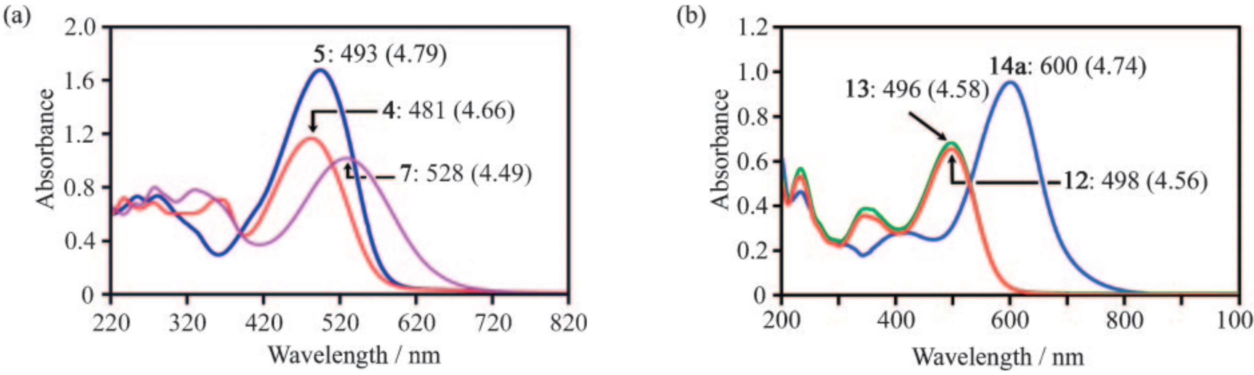


Figure 1. (a) UV–vis spectra of **4**, **5**, and **7** in CH_2Cl_2. Concentrations, **4**: 0.11 g L^{-1} (253 µmol L^{-1}), **5**: 0.12 g L^{-1} (268 µmol L^{-1}), and **7**: 0.14 g L^{-1} (322 µmol L^{-1}). Length of the cell, 0.1 cm each. Each log ε value is given in parenthesis. (b) UV–vis spectra of **12**, **13**, and **14a** in CH_3CN. Concentrations, **12**: 0.10 g L^{-1} (181 µmol L^{-1}), **13**: 0.10 g L^{-1} (177 µmol L^{-1}), and **14a**: 0.10 g L^{-1} (173 µmol L^{-1}). Length of the cell, 0.1 cm each. Each log ε value is given in parenthesis.

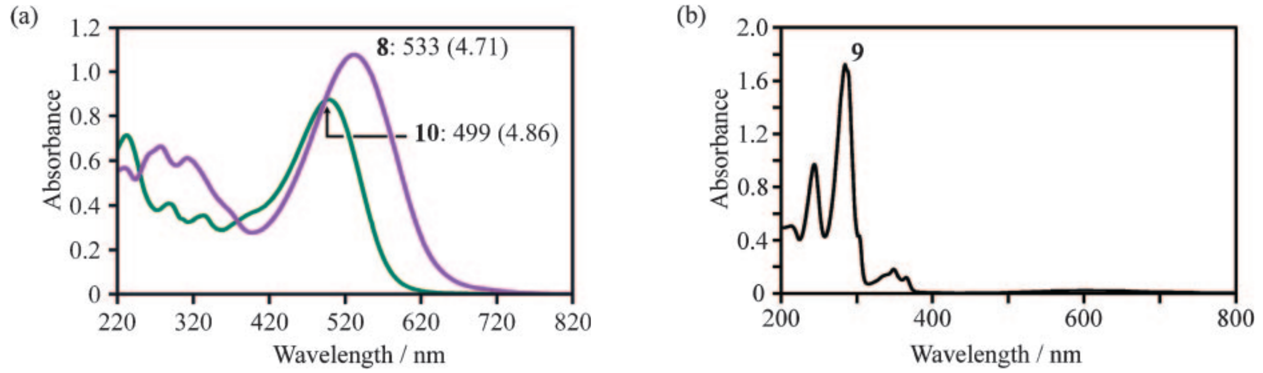


Figure 2. (a) UV–vis spectra of **8** in CH_2Cl_2 and **10** in CH_3CN. Concentrations, **8**: 0.13 g L^{-1} (123 µmol L^{-1}), **10**: 0.11 g L^{-1} (268 µmol L^{-1}). Length of the cell, 0.1 cm each. Each log ε value is given in parenthesis. (b) UV–vis spectrum of **9** in CH_3CN. Concentration, **9**: 0.075 g L^{-1} (379 µmol L^{-1}). Length of the cell, 0.1 cm. **9**: λ_{max}/nm (log ε), 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).

Compound **4** (71% yield) was obtained as dark green plates (mp 172 °C), while a solution of **4** in CH_2Cl_2 was red. The UV–vis spectrum is shown in Figure 1a. The characteristic UV–vis absorption bands resulting from guaiazulene (Figure 2b) were not observed and the longest absorption wavelength appeared at λ_{max} 481 nm (log $\varepsilon = 4.66$), indicating the formation of **4** with an extended π-electron system. Although the spectral pattern for the characteristic UV–vis absorption bands of **4** resembled those of the delocalized π-electron systems **12**[21] and **13**[21] (Chart 1), the longest absorption wavelength of **4** showed hypsochromic shifts (Δ 17 and 15 nm) and hyperchromic effects (Δ log $\varepsilon = 0.10$ and 0.08) in comparison with those of **12** and **13** (Figure 1b). The IR spectrum showed a specific band based on N=N at ν_{max} 1582 cm^{-1}, which was a low wavenumber shift ($\Delta\nu_{max}$ 19 cm^{-1} each) in comparison with those of **12**[21] and **13**.[21] The formula $C_{30}H_{30}ON_2$ was determined by exact EI-MS spectrum. The ^1H NMR spectrum showed signals resulting from a (*E*)-2-(3-guaiazulenyl)vinyl group and a 4-substituted 4′-methoxyazobenzene, the signals of which were carefully assigned using H–H COSY and computer-assisted simulation based on first-order analysis. The ^{13}C NMR spectrum exhibited 25 carbon signals assigned by HMQC and HMBC. Thus, the spectroscopic data for **4** led to the target structure illustrated in Chart 3. This reaction did not give the Z isomer (*E*)-4-{(*Z*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}-methoxybenzene.

Compound **5** (73% yield) was obtained as dark green plates (mp 233 °C), while similar to **4**, a solution of **5** in CH_2Cl_2 was red. The UV–vis spectrum is shown in Figure 1a. Comparative studies of the UV–vis spectrum of **5** with those of **4** and **9** showed that similar to **4**, no characteristic UV–vis absorption bands for **9** (Figure 2b) were observed, indicating the formation of **5** with an extended π-electron system. Although the spectral pattern for the characteristic UV–vis absorption bands of **5** resembled that of **4**, the longest absorption wavelength of **5** (λ_{max} 493 nm, log $\varepsilon = 4.79$) showed a bathochromic shift (Δ 12 nm) and a hyperchromic effect (Δ log $\varepsilon = 0.13$) in comparison with that of **4**. Furthermore, the spectral pattern for the characteristic UV–vis absorption bands of **5** resembled that of the delocalized π-electron system **14a**[21] (Chart 1), while the longest absorption wavelength of **5** showed a large hypsochromic shift (Δ 107 nm) and a slight hyperchromic effect (Δ log $\varepsilon = 0.05$) in comparison with that of **14a** (Figure 1b). The IR spectrum showed a specific band resulting from N=N at ν_{max} 1601 cm^{-1}, which was a high wavenumber shift ($\Delta\nu_{max}$ 19 cm^{-1}) in comparison with that of **4**; however, which was a low wavenumber shift ($\Delta\nu_{max}$ 19 cm^{-1}) in comparison with that of **14a**.[21] The molecular formula

$C_{31}H_{33}N_3$ was determined by exact FAB-MS spectrum. The ^{1}H NMR spectrum showed signals resulting from a (*E*)-2-(3-guaiazulenyl)vinyl group and a 4′-substituted 4-(dimethylamino)azobenzene, the signals of which were carefully assigned using similar techniques to those of **4**. The ^{13}C NMR spectrum exhibited 25 carbon signals assigned by HMQC and HMBC. Thus, the spectroscopic data for **5** led to the target structure illustrated in Chart 3. This reaction also did not give the Z isomer (*E*)-*N*,*N*-dimethyl-4-{(*Z*)-4-[2-(3-guaiazulenyl)vinyl]phenyldiazenyl}aniline.

^{1}H and ^{13}C NMR Spectral Parameters of 13 Compared with Those of 4. Comparative studies of the chemical shifts for the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **13**[21] (Chart 1) with those of the extended π-electron system **4** revealed that the Me-1′ proton signal (δ 2.51) for the 3-guaiazulenyl group of **13** showed an up-field shift in comparison with that of **4** (2.62) and the H-2′ proton signal (7.98) for the 3-guaiazulenyl group of **13** coincided with that of **4** (7.97). However, other 3-guaiazulenyl signals of **13** revealed down-field shifts in comparison with those of **4**. The order of larger down-field shift was H-5′ (Δδ 1.59) > H-6′ (1.13) > H-8′ (0.53) > Me$_2$C*H*-7′ (0.46) > Me-4′ (0.27) > (C*H*$_3$)$_2$CH-7′ (0.11). Although the (*C*H$_3$)$_2$CH-7′ carbon signal (δ 23.7) for the 3-guaiazulenyl group of **13** coincided with that of **4** (23.8), other 3-guaiazulenyl signals of **13** revealed down-field shifts in comparison with those of **4**. The order of larger down-field shift was C-7′ (Δδ 30.7) > C-5′ (23.4) > C-8a′ (21.0) > C-3a′ (20.9) > C-1′ (20.4) > C-3′ (15.5) > C-4′ (12.4) > C-6′ (10.1) > C-2′ (6.5) > C-8′ (6.4) > Me$_2$*C*H-7′ (3.0) > Me-4′ (1.6) > Me-1′ (1.5). The H-2″,6″, H-3″,5″, and MeO-4″ proton signals for the 4-substituted 4′-methoxyazobenzene unit of **13** coincided with those of **4**, however the other signals of **13** showed down-field shifts in comparison with those of **4**. The order of larger down-field shift was H-3,5 (Δδ 0.31) > H-2,6 (0.11). The C-1, C-2,6, C-3,5, C-1″, C-2″,6″, C-3″,5″, C-4″, and MeO-4″ carbon signals for the 4-substituted 4′-methoxyazobenzene part of **13** showed down-field shifts (Δδ 4.1, 1.2, 9.0, 1.0, 2.0, 1.7, 2.4, and 3.3 for C-1, C-2,6, C-3,5, C-1″, C-2″,6″, C-3″,5″, C-4″, and MeO-4″) in comparison with those of **4**, while the C-4 carbon signal for that of **13** revealed an up-field shift (Δδ 2.8) in comparison with that of **4**. Thus, an apparent difference between the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **13** and those of the extended π-electron system **4** was observed.

^{1}H and ^{13}C NMR Spectral Parameters of 14a Compared with Those of 5. Comparative studies of the chemical shifts for the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **14a**[21] with those of the extended π-electron system **5** showed broadening H-2″,6″ and H-3″,5″ proton signals of **14a**, which could not be unambiguously assigned, and further, the C-1, C-4, C-1″, C-2″,6″, C-3″,5″, and C-4″ carbon signals of **14a** were not observed, suggesting the existence of rotational stereoisomers for **14a″** (Chart 1), however the corresponding signals of **5** were observed. The Me-1′ proton signal (δ 2.53) for the 3-guaiazulenyl group of **14a** revealed a slight up-field shift in comparison with that of **5** (2.62), however other 3-guaiazulenyl signals of **14a** showed down-field shifts in comparison with those of **5**. The order of larger down-fieled shift was H-5′ (Δδ 1.61) > H-6′ (1.14) > H-8′ (0.57) > Me$_2$C*H*-7′ (0.47) > Me-4′ (0.28) > (C*H*$_3$)$_2$CH-7′ (0.11) > H-2′ (0.08). Although the (*C*H$_3$)$_2$CH-7′ carbon signal (δ 24.7) for the 3-guaiazulenyl group of **14a** coincided with that of **5** (24.4), other 3-guaiazulenyl signals of **14a** revealed down-field shifts in comparison with those of **5**. The order of larger down-field shift was C-7′ (Δδ 30.5) > C-5′ (23.4) > C-3a′ (21.2) > C-8a′ (20.7) > C-1′ (20.4) > C-3′ (14.8) > C-4′ (12.5) > C-6′ (10.5) > C-8′ (6.7) > C-2′ (6.3) > Me$_2$*C*H-7′ (3.2) > Me-4′ (1.9) > Me-1′ (1.7). The observed proton signals for the 4-(dimethylamino)azobenzene unit of **14a** showed that the H-2,6 proton signal (δ 7.85) coincided with that of **5** (7.83), while the H-3,5 proton signal (7.98) was a down-field shift relative to that of **5** (7.61). Although the C-2,6 carbon signal (δ 120.1) for the 4-(dimethylamino)azobenzene unit of **14a** was up-field compared to that of **5** (123.0), the C-3,5 and Me$_2$N-4″ carbon signals for that of **14a** showed down-field shifts in comparison with those of **5**. The order of larger down-field shift was C-3,5 (Δδ 10.3) > Me$_2$N-4″ (4.0). Thus, an apparent difference between the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **14a** and those of the extended π-electron system **5** was observed.

X-ray Crystal Structures of 4 and 5. The crystal structures of **4** and **5** were then determined by means of X-ray diffraction, producing accurate structural parameters. The ORTEP drawings of **4** and **5**, with a numbering scheme, indicating the molecular structures illustrated in Chart 3, are shown in Figures 3a and 3c along with selected bond lengths (Tables 1 and 2). As a result, it was found that from the dihedral angles between the least-squares planes, the planes of the 3-guaiazulenyl groups of **4** and **5** twisted by 15.9 and 10.0° from those of the –HCα=CβH–Ph functions, respectively. Furthermore, the plane of the (4-methoxyphenyl)diazenyl group of **4** twisted by 45.3° from that of another benzene ring, while that of the [4-(dimethylamino)phenyl]diazenyl group of **5** twisted by 9.9° from that of another benzene ring. The Cα=Cβ bond length of **4** (1.334 Å) coincided with that of **5** (1.331 Å). The average C–C bond length of the seven-membered ring for the 3-guaiazulenyl group of **4** (1.409 Å) coincided with that of **5** (1.410 Å). The C–C bond length of the five-membered ring for the 3-guaiazulenyl group of **4** appreciably varied between 1.359 and 1.495 Å; in particular, the C1′–C2′ bond length (1.359 Å) was characteristically shorter than the average C–C bond length for the five-membered ring (1.427 Å). Similar to **4**, the C–C bond length of the five-membered ring for the 3-guaiazulenyl group of **5** appreciably varied between 1.375 and 1.511 Å; in particular, the C1′–C2′ bond length (1.375 Å) was characteristically shorter than the average C–C bond length for the five-membered ring (1.435 Å). Although the N1=N2 bond length of **4** (1.265 Å) was longer than that of azobenzene[38–40] (**18**) (1.247 Å) (Chart 2), that of **5** (1.247 Å) coincided with that of **18** (Table 2). The N2–C1″ bond length of **4** (1.430 Å) coincided with that of **5** (1.433 Å) and **18** (1.428 Å), while the C1–N1 bond length of **4** (1.419 Å) was shorter than those of **5** (1.459 Å) and **18**. Thus, an apparent difference between the crystal structure of **4** and that of **5** was observed, owing to the influence of the substituted CH_3O– or $(CH_3)_2N$– group at the C4″ position of azobenzene. Along with the ORTEP drawings of **4** and **5**, the packing structures of **4** and **5** showed that each molecule formed a π-stacking structure in the single crystal,

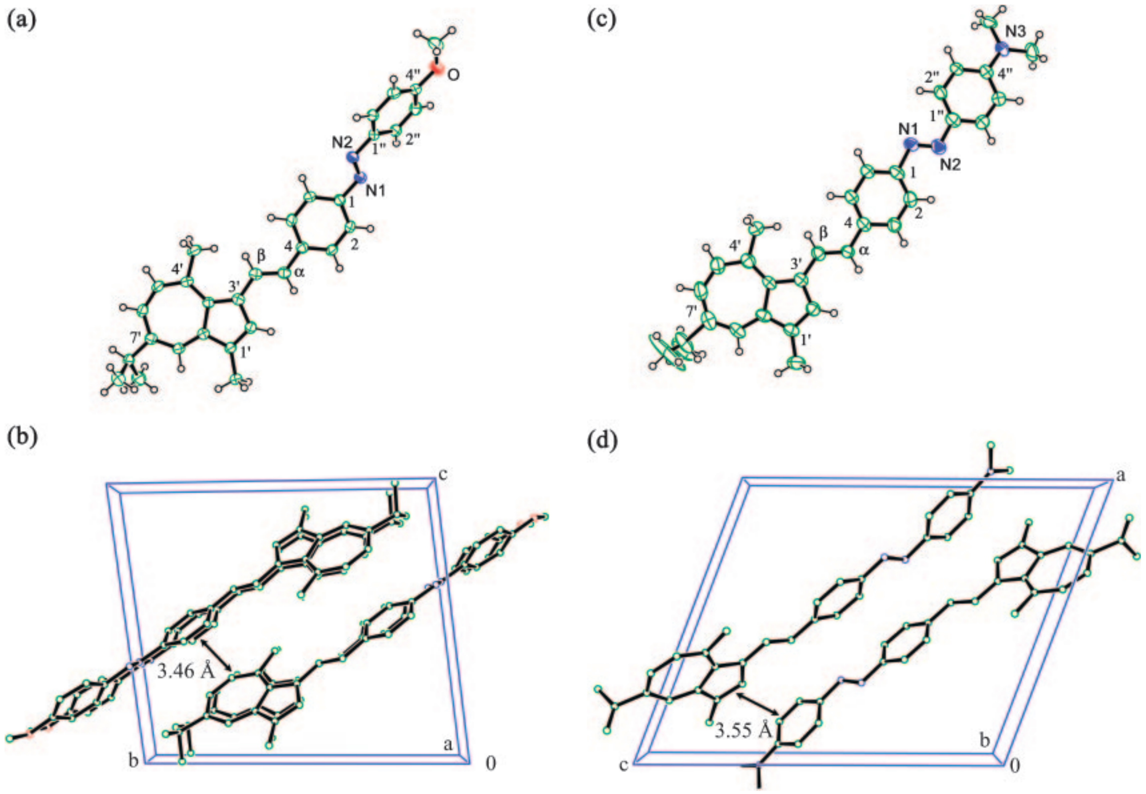


Figure 3. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **4** (a) and **5** (c), and the packing structures of **4** (b) and **5** (d); hydrogen atoms are omitted for reasons of clarity.

Table 1. The Selected C–C Bond Lengths (Å) for the 3-Guaiazulenylvinyl Groups of **4**, **5**, and **14b**

Atom	**4**	**5**	**14b**
C1′–C2′	1.359(4)	1.375(6)	1.348(6)
C2′–C3′	1.436(4)	1.430(7)	1.442(6)
C3′–C3a′	1.416(4)	1.437(7)	1.503(6)
C3a′–C4′	1.410(4)	1.393(8)	1.390(6)
C4′–C5′	1.399(4)	1.398(7)	1.407(6)
C5′–C6′	1.383(4)	1.401(8)	1.379(7)
C6′–C7′	1.389(4)	1.390(10)	1.412(6)
C7′–C8′	1.397(4)	1.386(9)	1.382(6)
C8′–C8a′	1.385(4)	1.386(7)	1.399(6)
C8a′–C1′	1.428(4)	1.416(8)	1.446(6)
C3a′–C8a′	1.495(4)	1.511(7)	1.445(6)
C3′–Cβ	1.442(4)	1.442(7)	1.360(6)[a]
Cα–Cβ	1.334(4)	1.331(7)	—

a) C3′–Cα (see Chart 2).

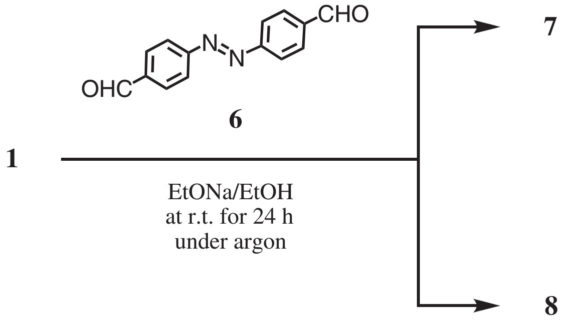
Table 2. The Selected Bond Lengths (Å) for the Azobenzene of **4**, **5**, **14b**, and **18**

Atom	**4**[a]	**5**[a]	**14b**[a]	**18**
Cα–C4	1.460(4)	1.461(7)	1.439(6)	—
C4–C5	1.408(4)	1.365(8)	1.405(6)	1.382(3)
C5–C6	1.384(4)	1.387(7)	1.377(6)	1.384(3)
C6–C1	1.400(4)	1.368(8)	1.393(6)	1.387(2)
C1–C2	1.387(4)	1.371(8)	1.403(6)	1.389(2)
C2–C3	1.380(4)	1.393(7)	1.375(6)	1.384(3)
C3–C4	1.396(4)	1.415(8)	1.405(6)	1.391(2)
C1–N1	1.419(4)	1.459(6)	1.400(5)	1.428(2)
N1–N2	1.265(3)	1.247(6)	1.299(5)	1.247(2)
N2–C1″	1.430(4)	1.433(6)	1.324(6)	—
C1″–C2″	1.392(4)	1.384(8)	1.423(6)	—
C2″–C3″	1.373(4)	1.378(7)	1.335(6)	—
C3″–C4″	1.390(4)	1.407(8)	1.446(6)	—
C4″–C5″	1.378(4)	1.380(8)	1.431(7)	—
C5″–C6″	1.398(4)	1.376(7)	1.349(7)	—
C6″–C1″	1.383(4)	1.361(8)	1.438(6)	—
C4″–N3	—	1.381(6)	1.341(6)	—

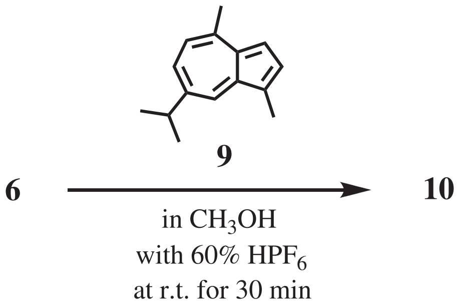
a) For a comparative purpose, the numbering schemes of the azobenzene of **4**, **5**, and **14b** were changed as shown in Charts 2 and 3.

and revealed that each average inter-plane distance between the overlapping molecules, which were overlapped so that those dipole moments might be negated mutually, was 3.46 Å for **4** (Figure 3b) and 3.55 Å for **5** (Figure 3d). Moreover, comparing the selected bond lengths of **14b**[21] (Chart 2) to those of structurally related compounds **4** and **5** are shown in Tables 1 and 2. As a result, it was found that the 3-guaiazulenylmethylium ion of **14b** clearly underwent bond alternation between single and double bonds, indicating the formation of a similar resonance structure to **14a′** (Chart 1), and the 4-[4-(dimethylamino)phenyldiazenyl]phenyl group also clearly underwent bond alternation between the single and double bonds, indicating the formation of a similar resonance structure to **14a″** (Chart 1).

Preparation and Spectroscopic Properties of 7 and 8. The target extended π-electron systems **7** and **8** were prepared using the Wittig reaction shown in Scheme 3. The structures of



Scheme 3. The reaction of **1** with **6** in ethanol in the presence of sodium ethoxide at 25 °C for 24 h under argon, affording the corresponding azobenezene derivatives **7** and **8**.



Scheme 4. The reaction of **6** with **9** in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min, affording the corresponding dicarbenium ion compound **10**.

the products were established on the basis of similar spectroscopic analyses to those of **4** and **5**.

Compound **7** (7% yield) was obtained as dark green prisms (mp 172 °C), while a solution of **7** in CH_2Cl_2 was reddish-violet. The UV–vis spectrum is shown in Figure 1a. Although the spectral pattern of **7** resembled those of **4** and **5** (Figure 1a), the longest absorption wavelength of **7** (λ_{max} 528 nm, $\log \varepsilon = 4.49$) showed bathochromic shifts (Δ 47 and 35 nm) and hypochromic effects ($\Delta \log \varepsilon = 0.17$ and 0.30) in comparison with those of **4** and **5**. The IR spectrum showed specific bands resulting from C=O at 1701 cm^{-1} and N=N at 1585 cm^{-1} which coincided with that of **4**. The molecular formula $C_{30}H_{28}ON_2$ was determined by exact FAB-MS spectrum. The ^{1}H NMR spectrum showed signals resulting from a (*E*)-2-(3-guaiazulenyl)vinyl group and a 4′-substituted azobenzene-4-carbaldehyde, the signals of which were carefully assigned using H–H COSY and computer-assisted simulation based on first-order analysis. The ^{13}C NMR spectrum exhibited 25 carbon signals assigned by HMQC and HMBC. Thus, the spectroscopic data for **7** led to the diazene structure illustrated in Chart 3.

Compound **8** (24% yield) was obtained as a dark green powder (mp 263 °C), while similar to **7**, a solution of **8** in CH_2Cl_2 was reddish-violet. The UV–vis spectrum is shown in Figure 2a. The characteristic UV–vis absorption bands for **9** (Figure 2b) were not observed, suggesting the formation of **8** with an extended π-electron system. The longest absorption wavelength of **8** (λ_{max} 533 nm, $\log \varepsilon = 4.71$) showed a slight bathochromic shift (Δ 5 nm) and a hyperchromic effect ($\Delta \log \varepsilon = 0.22$) in comparison with that of **7**. The IR spectrum showed specific bands resulting from N=N at 1585 cm^{-1}, whose wavenumber coincided with that of **7**. The molecular formula $C_{46}H_{46}N_2$ was determined by exact FAB-MS spectrum. The ^{1}H NMR spectrum showed signals originating from two equivalent (*E*)-2-(3-guaiazulenyl)vinyl groups and a 4,4′-substituted azobenzene, the signals of which were carefully assigned using similar spectroscopic analyses to those of **7**. The ^{13}C NMR spectrum exhibited 20 carbon signals assigned by HMQC and HMBC. Thus, the spectroscopic data for **8** led to the target structure illustrated in Chart 3.

Preparation and Spectroscopic Properties of 10. For comparative purposes of the spectroscopic properties of the delocalized π-electron system **10** with those of the extended π-electron system **8**, the target compound **10** was prepared according to Scheme 4. The structure of the product **10** was established on the basis of elemental analysis and similar spectroscopic analyses to **8**.

Compound **10** (46% yield) was obtained as dark red prisms (decomp >178 °C). The UV–vis spectrum is shown in Figure 2a. Although the spectral pattern of **10** resembled that of **8**, the longest absorption wavelength of **10** (λ_{max} 499 nm, $\log \varepsilon = 4.86$) showed a hypsochromic shift (Δ 34 nm) and a hyperchromic effect ($\Delta \log \varepsilon = 0.15$) in comparison with that of **8**. The IR spectrum showed specific bands originating from N=N at 1601 cm^{-1}, which was a high wavenumber shift ($\Delta \nu_{max}$ 16 cm^{-1}) in comparison with that of **8**, and counter anion (PF_6^-) at 837 and 556 cm^{-1}, the wavenumbers of which coincided with those of **12**–**14a**.[21] The formula $C_{44}H_{44}N_2$ for the dicarbenium ion part was determined by exact FAB-MS spectrum. An elemental analysis confirmed $C_{44}H_{44}N_2F_{12}P_2$. The ^{1}H NMR spectrum showed signals originating from two equivalent 3-guaiazulenylmethylium ion structures, and revealed signals resulting from a 4,4′-substituted azobenzene, the signals of which were carefully assigned using similar techniques to those of **8**. The ^{13}C NMR spectrum exhibited 19 carbon signals assigned by HMQC and HMBC. Thus, the elemental analysis and the spectroscopic data for **10** led to the target structure illustrated in Chart 4.

Reduction of 10 with $NaBH_4$ and ^{1}H and ^{13}C NMR Spectral Parameters of 10 Compared with Those of 11. For comparative purposes of the ^{1}H and ^{13}C NMR properties of the delocalized π-electron system **10** with those of the non-conjugated π-electron system **11** which have two 3-guaiazulenyl groups and an azobenzene unit (Chart 4), the target compound **11** was prepared. Namely, the reduction of **10** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 88% yield of diazene **11**, in which a hydride ion attached to the two HC^+-α carbon atoms of **10**, selectively. Comparative studies of the chemical shifts for the ^{1}H and ^{13}C NMR signals of **10** with those of **11** showed that the Me-1′ proton signal for the 3-guaiazulenyl group of **10** revealed a slight up-field shift ($\Delta\delta$ 0.08) in comparison with that of **11**, however other 3-guaiazulenyl signals of **10** showed down-field shifts in comparison with those of **11**. The order of larger down-field shift was H-5′ ($\Delta\delta$ 1.76) > H-6′ (1.17) > H-2′ (0.62) > Me-4′ (0.57) > H-8′ (0.49) > Me_2CH-7′ (0.48) > $(CH_3)_2CH$-7′ (0.12). Although the C-2′ and $(CH_3)_2CH$-7′

carbon signals for the 3-guaiazulenyl group of **10** coincided with those of **11**, other 3-guaiazulenyl signals of **10** showed down-field shifts in comparison with those of **11**. The order of larger down-field shift was C-7′ ($\Delta\delta$ 33.9) > C-5′ (25.4) > C-8a′ (24.5) > C-1′ (23.3) > C-3a′ (21.0) > C-3′ (17.3) > C-4′ (13.4) > C-6′ (11.0) > C-8′ (7.0) > Me-4′ (3.6) > Me$_2$*C*H-7′ (3.0) > Me-1′ (1.7). The H-2,6 proton signal for the 4,4′-substituted azobenzene part of **10** showed a slight down-field shift ($\Delta\delta$ 1.0) in comparison with that of **11**; however, the H-3,5 proton signal for that of **10** revealed a large down-field shift ($\Delta\delta$ 0.89) in comparison with that of **11**. The C-1 and C-3,5 carbon signals for the 4,4′-substituted azobenzene of **10** showed down-field shifts ($\Delta\delta$ 3.8 and 6.6 for C-1 and C-3,5) in comparison with that of **11**, while the C-2,6 and C-4 carbon signals for that of **10** revealed up-field shift ($\Delta\delta$ 0.6 and 5.2 for C-2,6 and C-4) in comparison with that of **11**. Comparing the ^{1}H and ^{13}C NMR chemical shifts of **10** to those of **11**, an apparent difference between the ^{1}H and ^{13}C NMR chemical shifts of the delocalized π-electron system **10** and those of the hydride reduction product **11** was observed.

^{1}H and ^{13}C NMR Spectral Parameters of 10 Compared with Those of 8. Comparative studies of the chemical shifts for the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **10** with those of the extended π-electron system **8** revealed that the Me-1′ proton signal (δ 2.53) for the 3-guaiazulenyl group of **10** showed a slight up-field shift in comparison with that of **8** (2.62), however other 3-guaiazulenyl signals of **10** revealed down-field shifts in comparison with those of **8**. The order of larger down-field shift was H-5′ ($\Delta\delta$ 1.65) > H-6′ (1.16) > H-8′ (0.57) > Me$_2$C*H*-7′ (0.49) > Me-4′ (0.30) > (C*H*$_3$)$_2$CH-7′ (0.12) > H-2′ (0.04). Although the (*C*H$_3$)$_2$CH-7′ carbon signal for the 3-guaiazulenyl group of **10** coincided with that of **8**, other 3-guaiazulenyl signals of **10** revealed down-field shifts in comparison with those of **8**. The order of larger down-field shift was C-7′ ($\Delta\delta$ 31.2) > C-5′ (23.7) > C-8a′ (21.2) > C-1′,3a′ (20.8, each) > C-3′ (16.1) > C-4′ (12.6) > C-6′ (10.6) > C-8′ (6.5) > C-2′ (6.0) > Me$_2$*C*H-7′ (2.9) > Me-1′,4′ (1.5, each). All the proton signals for the 4,4′-substituted azobenzene of **10** showed down-field shifts in comparison with those of **8**. The order of larger down-field shift was H-3,5 ($\Delta\delta$ 0.38) > H-2,6 (0.23). The C-1, C-2,6, and C-3,5 carbon signals for the 4,4′-substituted azobenzene of **10** showed down-field shifts ($\Delta\delta$ 3.6, 1.6, and 8.8 for C-1, C-2,6, and C-3,5) in comparison with that of **8**, while the C-4 carbon signal for that of **10** revealed up-field shift ($\Delta\delta$ 1.6) in comparison with that of **8**. Thus, an apparent difference between the ^{1}H and ^{13}C NMR signals of the delocalized π-electron system **10** and those of the extended π-electron system **8** was observed.

Conclusion

We have reported the following five interesting points in this paper. namely: (i) The Wittig reactions of diazenes **2** and **3** with (3-guaiazulenylmethyl)triphenylphosphonium bromide in ethanol in the presence of sodium ethoxide at 25 °C for 24 h under argon gave only E forms **4** and **5** in 71 and 73% yields. The reactions did not give the Z isomers. (ii) Comparing the spectroscopic properties of the two new extended π-electron systems **4** and **5** to those of structurally related (and delocalized) π-electron systems **13** and **14a**, an apparent difference between the spectroscopic properties of **4** and **5** and those of the delocalized π-electron systems **13** and **14a** was reported and further, the crystal structural parameters of **14b** compared with those of **4** and **5** apparently supported the formation of **14b** with similar resonance structures to those of **14a** (Chart 1) in the single crystal. (iii) The Wittig reaction of diazene **6** with the same reagent under the same reaction conditions as the above afforded only E forms **7** and **8** in 7 and 24% yields. The reaction also did not give the Z isomers. (iv) The reaction of guaiazulene (**9**) with **6** in methanol in the presence of hexafluorophosphoric acid at 25 °C for 30 min provided **10** in 46% yield which upon reduction with NaBH$_4$ gave diazene **11** in 88% yield, in which a hydride ion attached to the two HC$^+$-α carbon atoms of **10** selectively. (v) Similar to (ii), comparing the spectroscopic properties of a new extended π-electron system **8** to those of a new delocalized π-electron system **10**, an apparent difference between the spectroscopic properties of **8** and those of **10** was documented.

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32 The Wittig reagent **1** was prepared according to the following procedures: To a powder of $NaBH_4$ (30 mg, 793 µmol) was added a solution of guaiazulene-3-carbaldehyde[33] (90 mg, 397 µmol) in ethanol (1.5 mL). The mixture was stirred at 25 °C for 1 h. After the reaction, distilled water (10 mL) was added to the mixture and then the resulting product was extracted with dichloromethane (10 mL × 3). The extract was washed with distilled water, dried (Na_2SO_4), and evaporated in vacuo to provide 3-guaiazulenylmethanol as a blue paste. To a solution of 3-guaiazulenylmethanol in chloroform (3 mL) was added a solution of triphenylphosphonium bromide (130 mg, 378 µmol) in chloroform (3 mL). The mixture was refluxed for 1 h under argon. After cooling, the reaction mixture was poured into diethyl ether (10 mL) and then was centrifuged at 2.5 krpm for 1 min. The obtained product was carefully washed with diethyl ether to provide pure **1** as a blue powder (195 mg, 352 µmol, 93% yield).

33 Guaiazulene-3-carbaldehyde was prepared according to the following procedures: To a solution of commercially available guaiazulene (**9**) (100 mg, 504 µmol) in *N*,*N*-dimethylformamide (DMF) (3.0 mL) was added a solution of phosphoryl chloride (100 µL). The mixture was stirred at 0 °C for 1 h. After the reaction, the reaction solution was carefully neutralized with aq KOH and then the resulting product was extracted with dichloromethane (10 mL × 3). The extract was washed with distilled water, dried (Na_2SO_4), and evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate (3:2, v/v). The crude product was recrystallized from hexane to provide pure guaiazulene-3-carbaldehyde as stable crystals (108 mg, 477 µmol, 94% yield).

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