Preparation, Crystal Structures, and Properties of New Conjugated π-Electron Systems with 3-Guaiazulenyl and 4-(Dimethylamino)phenyl Groups

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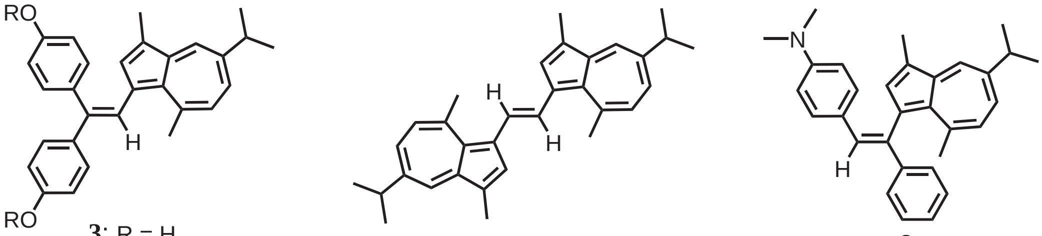
Reaction of guaiazulene with 1,2-bis[4-(dimethylamino)phenyl]-1,2-ethanediol in methanol in the presence of hydrochloric acid at 60 °C for 3 h gives 1,1-bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene, in 81% yield, via pinacol rearrangement and further Wittig reaction of 3-formylguaiazulene with [4-(dimethylamino)benzyl]triphenylphosphonium bromide in ethanol containing NaOEt at 25 °C for 24 h under argon affords (*E*)-2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene in 12% yield. Crystal structures as well as spectroscopic and electrochemical properties of the products, with a view to comparative study, are reported. Moreover, reactions of the products with 2 equiv of tetracyanoethylene (TCNE) in benzene at 25 °C for 24 h under argon give 1,1,2,2,11,11,12,12-octacyano-3,3-bis[4-(dimethylamino)phenyl]-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene and 1,1,2,2,11,11,12,12-octacyano-3-[4-(dimethylamino)phenyl]-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene in 74 and 41% yields. A plausible reaction pathway for the formation of the unique products, possessing interesting structures, is submitted.

Azulene and its derivatives have been studied to a considerable extent over the past 50 years and an extremely large number of the studies have been well documented and further, naturally occurring guaiazulene (=7-isopropyl-1,4-dimethylazulene, **1**) has been widely used clinically as an antiinflammatory and antiulcer agent. However, none have really been used as other industrial materials. As a series of basic studies on creation and potential utility of novel functional materials with a 3-guaiazulenyl (=7-isopropyl-1,4-dimethyl-3-azulenyl) (or another 1-azulenyl) group possessing a large dipole moment, 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 expanded π-electron systems with a 3-guaiazulenyl (or a 1-azulenyl) group.[1–16] During the course of investigation, we found that **3**–**5**[8] and **6**[8] (Chart 1) serve as strong electron donors and electron acceptors and **3**–**5** undergo stepwise two-electron oxidation by means of CV and DPV, while (*Z*)-4-(dimethylamino)phenyl-substituted compound **6** undergoes two-electron oxidation simultaneously. Furthermore, we found that reaction of **5** and **4** with 2 equiv of TCNE, which serves as a strong electron acceptor,[11,12] in benzene at 25 °C for 24 h under argon gives **16**[12] and **17**[12] (Chart 2), selectively. Along with the above basic studies, our interest has quite recently been focused on the following five points for comparative purposes: namely, (i) studies of 1,1-bis[4-(dimethylamino)phenyl]-substituted compound **9** (Figure 1) and (*E*)-4-(dimethylamino)phenyl-substituted compound **13** (Figure 2) compared with those of **6**. These compounds can be expected to serve as a strong three- (or two-) electron donor for **9** (or **13**) and one-electron acceptors; (ii) investigation of a plausible electron-transfer mechanism based on the redox potentials of **9** and **13**, compared with those of **6**, by means of CV and DPV; (iii) the reactions of **9** and **13** with TCNE under the same reaction conditions as for **4** and **5**, probably yielding new **17** and **16** analogues **18** and **19** (Figure 10);



3: R = H
4: R = CH_3

5

6

Chart 1.

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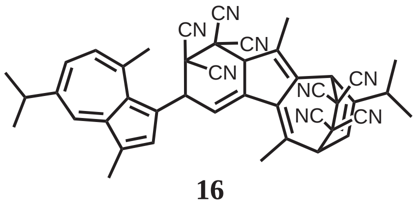

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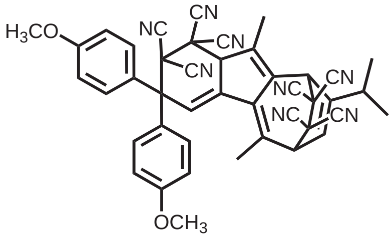

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Chart 2.

(iv) accurate crystal structure determination of **18** and **19**. Because the crystal structure of **16** was determined by means of X-ray diffraction, accurate structural parameters could not be obtained because of difficulty in obtaining a stable single crystal suitable for X-ray crystallographic analysis[12] and further, the crystal structure of **17** has not yet been achieved for similar reasons; and (v) investigation of a plausible reaction pathway for the formation of the resulting products **16**–**19**. We now wish to report the detailed studies on the above five points (i)–(v).

Experimental

General. Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN coder. FAB-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 at 25 °C. The ^{1}H NMR spectra were assigned using computer-assisted simulation analysis (software: gNMR developed by Adept Scientific plc) on a DELL Dimension XPS T500 personal computer with a Pentium III processor. Cyclic and differential pulse voltammograms (CV and DPV) were measured by an ALS Model 600 electrochemical analyzer.

Preparation of 1,1-Bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene (9). To a solution of commercially available guaiazulene (**1**) (50 mg, 253 µmol) in methanol (1.5 mL) was added a solution of 1,2-bis[4-(dimethylamino)phenyl]-1,2-ethanediol[17] (**8**) (80 mg, 267 µmol) in methanol (1.5 mL) containing 36% hydrochloric acid (0.2 mL). The mixture was stirred at 60 °C for 3 h. After the reaction, distilled water was added to the mixture and the resulting product was extracted with diethyl ether (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 (several times) with hexane–ethyl acetate–benzene (7:2:1, vol/vol/vol) as an eluant. The crude product was recrystallized from dichloromethane–hexane (1:5, vol/vol) to provide pure **9** (95 mg, 206 µmol, 81% yield) as stable crystals.

Compound **9**: Dark-green plates [$R_f = 0.48$ on silica-gel TLC (solv. hexane:ethyl acetate:benzene = 7:2:1, vol/vol/vol)]; mp 201 °C [determined by thermal analysis (TGA and DTA)]; found: C, 85.73; H, 8.37; N, 6.02%, calcd for $C_{33}H_{38}N_2$: C, 85.67; H, 8.28; N, 6.05%; UV–vis $\lambda_{\max}$ (CH_3CN) nm (log ε): 204 (4.73), 225 (4.47), 253 (4.50), 287 (4.62), 330sh (4.47), 391 (4.41), and 647 (2.69); IR $\nu_{\max}$ (KBr) cm^{-1}: 2955–2797 (C–H), 1609, 1520 (C=C), and 1358 (C–N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 462.3050; calcd for $C_{33}H_{38}N_2$: M^+, m/z 462.3035; ^{1}H NMR (benzene-d_6): signals based on the 3-guaiazulenyl group: δ 1.73 (6H, d, $J = 7.0$ Hz, $(CH_3)_2$CH-7‴), 2.31 (3H, s, Me-1‴), 2.70 (1H, sept, $J = 7.0$ Hz, $(CH_3)_2$CH-7‴), 3.00 (3H, s, Me-4‴), 6.59 (1H, d, $J = 10.5$ Hz, H-5‴), 7.00 (1H, dd, $J = 10.5$, 2.5 Hz, H-6‴), 7.60 (3H, s, H-2‴), and 7.88 (1H, d, $J = 2.5$ Hz, H-8‴); signals based on the two 4-(dimethylamino)phenyl groups: δ 2.45 (6H, s, $(CH_3)_2$N-4′), 2.54 (6H, s, $(CH_3)_2$N-4″), 6.51 (2H, dd, $J = 8.5$, 2.5 Hz, H-3′,5′), 6.67 (2H, dd, $J = 8.5$, 2.5 Hz, H-3″,5″), 7.54 (2H, dd, $J = 8.5$, 2.5 Hz, H-2′,6′), and 7.66 (2H, dd, $J = 8.5$, 2.5 Hz, H-2″,6″); and a signal based on the >C=CH– part: δ 7.81 (1H, s, H-2); ^{13}C NMR (benzene-d_6): δ 150.2 (C-4″), 149.6 (C-4′), 146.3 (C-4‴), 140.8 (C-2‴), 139.9 (C-8a‴), 139.6 (C-7‴), 135.2 (C-3a‴), 134.3 (C-6‴), 134.1 (C-2″,6″), 133.9 (C-1′), 133.0 (C-2′,6′), 132.8 (C-8‴), 129.9 (C-1″), 128.3 (C-3‴), 126.0 (C-5‴), 125.4 (C-2), 125.0 (C-1‴), 123.3 (C-1), 112.8 (C-3″,5″), 112.5 (C-3′,5′), 40.3 ($(CH_3)_2$N-4″), 40.0 ($(CH_3)_2$N-4′), 37.9 (Me_2CH-7‴), 27.8 (Me-4‴), 24.5 ($(CH_3)_2$CH-7‴), and 12.9 (Me-1‴).

X-ray Crystal Structure of 1,1-Bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene (9). A total of 6527 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 198 K. The structure was solved by direct methods (SIR92[18]) and expanded using Fourier techniques (DIRDIF94[19]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package.[20] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center: Deposition number CCDC-621672 for compound No. 9. 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 Center, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for **9**: $C_{33}H_{38}N_2$ (FW: 462.68), dark-green prism (the crystal size, 0.50 × 0.30 × 0.50 mm^3), triclinic, $P\bar{1}$ (#2), $a = 10.589(2)$ Å, $b = 15.368(2)$ Å, $c = 8.768(1)$ Å, $\alpha = 95.78(1)°$, $\beta = 105.56(1)°$, $\gamma = 79.47(1)°$, $V = 1349.5(4)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.139$ g cm^{-3}, μ(Mo Kα) = 0.66 cm^{-1}, scan width: $(1.21 + 0.30 \tan\theta)°$, scan mode: ω–2θ, scan rate: 16.0° min^{-1}, measured reflections: 6527, observed reflections: 5513, No. of parameters: 316, $R1 = 0.057$, $wR2 = 0.177$, and goodness of fit indicator: 1.92.

Preparation of (*E*)-2-[4-(Dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene (13). To a solution of 3-formylguaiazulene[21,22] (**2**) (50 mg, 221 µmol) in ethanol (2 mL) was added a solution of [4-(dimethylamino)benzyl]triphenylphosphonium bromide[23–25] (**12**) (121 mg, 254 µmol) in ethanol (2 mL) containing sodium ethoxide (18 mg, 265 µmol). The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled water was added to the mixture and the resulting product was extracted with dichloromethane (20 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 (4:1, vol/vol) as an eluant. The crude product was recrystallized from ethanol to provide pure **13** (9 mg, 26 µmol, 12% yield) as stable crystals.

Compound **13**: Dark-green plates [$R_f = 0.60$ on silica-gel TLC (solv. hexane:ethyl acetate:benzene = 7:2:1, vol/vol/vol)]; mp 155 °C [determined by thermal analysis (TGA and DTA)]; found: C, 87.56; H, 8.56; N, 4.08%, calcd for $C_{25}H_{29}N$: C, 87.41; H, 8.51; N, 4.08%; UV–vis $\lambda_{\max}$ (CH_3CN) nm ($\log \varepsilon$): 228 (4.39), 246 (4.33), 287 (4.41), 333 (4.59), 421 (4.61), and 654 (2.80); IR $\nu_{\max}$ (KBr) cm^{-1}: 2955–2800 (C–H), 2955, 949 (–HC=CH–), 1612, 1520 (C=C), and 1358 (C–N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 343.2298; calcd for $C_{25}H_{29}N$: M^+, m/z 343.2300; ^1H NMR (benzene-d_6): signals based on the 3-guaiazulenyl group: δ 1.20 (6H, d, $J = 7.2$ Hz, $(CH_3)_2CH$-7′), 2.56 (3H, s, Me-1′), 2.73 (1H, sept, $J = 7.2$ Hz, $(CH_3)_2CH$-7′), 2.88 (3H, s, Me-4′), 6.56 (1H, d, $J = 10.6$ Hz, H-5′), 7.00 (1H, dd, $J = 10.6, 2.0$ Hz, H-6′), 7.97 (1H, d, $J = 2.0$ Hz, H-8′), and 8.01 (1H, s, H-2′); signals based on the 4-(dimethylamino)phenyl group: δ 2.56 (6H, s, $(CH_3)_2N$-4″), 6.67 (2H, dd, $J = 8.5, 2.5$ Hz, H-3″,5″), and 7.57 (2H, dd, $J = 8.5, 2.5$ Hz, H-2″,6″); and signals based on the *trans*-HC=CH– part: δ 7.15 (1H, d, $J = 16.0$ Hz, H-2) and 8.10 (1H, d, $J = 16.0$ Hz, H-1); ^{13}C NMR (benzene-d_6): δ 149.9 (C-4″), 146.2 (C-4′), 141.2 (C-8a′), 140.1 (C-7′), 136.7 (C-2′), 134.6 (C-6′), 133.4 (C-8′), 132.7 (C-3a′), 128.4 (C-3′,1″), 128.0 (C-2), 127.4 (C-2″,6″), 126.9 (C-5′), 126.1 (C-1′), 123.0 (C-1), 113.2 (C-3″,5″), 40.2 ($(CH_3)_2N$-4″), 37.9 ($(CH_3)_2CH$-7′), 28.4 (Me-4′), 24.5 ($(CH_3)_2CH$-7′), and 13.1 (Me-1′).

X-ray Crystal Structure of (*E*)-2-[4-(Dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene (13). A total of 5125 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 198 K. The structure was solved by direct methods (SIR92[18]) and expanded using Fourier techniques (DIRDIF94[19]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package.[20] Deposition number CCDC-621951 for compound No. 13.

Crystallographic data for **13**: $C_{25}H_{29}N$ (FW: 343.51), dark-green prism (the crystal size, $0.50 \times 0.30 \times 0.50$ mm^3), monoclinic, $P2_1/n$ (#14), $a = 14.545(8)$ Å, $b = 9.325(7)$ Å, $c = 16.495(8)$ Å, $\beta = 114.79(4)°$, $V = 2031(2)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.123$ g cm^{-3}, μ(Mo Kα) = 0.64 cm^{-1}, scan width: $(1.21 + 0.30 \tan\theta)°$, scan mode: ω–2θ, scan rate: 16.0° min^{-1}, measured reflections: 5125, observed reflections: 3928, No. of parameters: 235, $R1 = 0.073$, $wR2 = 0.216$, and goodness of fit indicator: 1.95.

Preparation of 1-[4-(Dimethylamino)phenyl]-2-phenyl-1,2-ethanedione (15). To a solid of copper sulfate (505 mg, 3.17 mmol) was added a solution of commercially available 4-(dimethylamino)benzoin (**14**) (304 mg, 1.19 mmol) in a mixed solvent of pyridine (2 mL) and distilled water (2 mL). The mixture was refluxed for 5 h and cooled, precipitating a yellow solid, and was then centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was washed with distilled water and hexane, and was recrystallized from ethanol (several times) to provide pure **15** as stable crystals (237 mg, 0.94 mmol, 79% yield).

Compound **15**: Yellow blocks [$R_f = 0.15$ on silica-gel TLC (solve. hexane:ethyl acetate = 4:1, vol/vol)]; mp 114 °C [determined by thermal analysis (TGA and DTA)]; found: C, 75.39; H, 6.25; N, 5.52%, calcd for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53%; exact EI-MS, found: m/z 253.1096, calcd for $C_{16}H_{15}O_2N$: M^+, 253.1143.

X-ray Crystal Structure of 1-[4-(Dimethylamino)phenyl]-2-phenyl-1,2-ethanedione (15). A total of 3475 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 296 K. The structure was solved by direct methods (SIR97[26]) and expanded using Fourier techniques (DIRDIF94[19]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package.[20] Deposition number CCDC-225122 for compound No. 15.

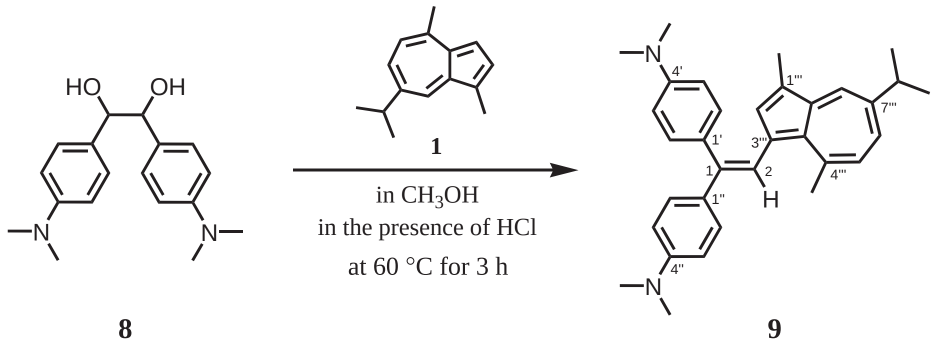
Crystallographic data for **15**: $C_{16}H_{15}O_2N$ (FW: 253.30), yellow prism (the crystal size, $0.80 \times 0.60 \times 0.20$ mm^3), monoclinic, $P2_1/c$ (#14), $a = 13.010(3)$ Å, $b = 7.710(4)$ Å, $c = 14.234(2)$ Å, $\beta = 109.14(1)°$, $V = 1348.9(7)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.247$ g cm^{-3}, μ(Mo Kα) = 0.82 cm^{-1}, scan width: $(1.47 + 0.30 \tan\theta)°$, scan mode: ω–2θ, scan rate: 8.0° min^{-1}, measured reflections: 3475, observed reflections: 1773, No. of parameters: 172, $R1 = 0.042$, $wR2 = 0.119$, and goodness of fit indicator: 1.15.

Reaction of 1,1-Bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene (9) with Tetracyanoethylene (TCNE). To a solution of 1,1-bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene (**9**) (20 mg, 43 µmol) in benzene (1.5 mL) was added a solution of TCNE (11 mg, 86 µmol) in benzene (1.5 mL) under argon, turning the dark-green solution into a black solution, rapidly. The mixture was stirred at 25 °C for 24 h under argon, gradually giving a white precipitate of **18** and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with benzene and hexane, and was recrystallized from ethyl acetate–hexane (1:5, vol/vol) to provide pure **18** (23 mg, 32 µmol, 74% yield) as stable crystals.

Compound **18**: Pale-green plates; mp 147 °C [determined by thermal analysis (TGA and DTA)]; UV–vis $\lambda_{\max}$ (ethyl acetate) nm ($\log \varepsilon$): 270 (4.64), 284 (4.63), and 390 (4.11); IR $\nu_{\max}$ (KBr) cm^{-1}: 2253 and 2249 (C≡N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 719.3324; calcd for $C_{45}H_{39}N_{10}$: $[M + H]^+$, m/z 719.3359. The relative intensity of the ^1H NMR signals for the diastereomers **18a** and **18b** showed a ration of ca. 7:5.

Compound **18a**: ^1H NMR (THF-d_8): δ 1.14, 1.15 (3H each, d, $J = 6.7$ Hz, $(CH_3)_2CH$-8), 2.41 (3H, br s, Me-10), 2.43 (3H, br s, Me-5), 2.61 (1H, sept d, $J = 6.7, 0.8$ Hz, $(CH_3)_2CH$-8), 4.11 (1H, d, $J = 7.9$ Hz, H-6), 4.51 (1H, br q, H-10a), 4.68 (1H, d, $J = 1.3$ Hz, H-9), 6.42 (1H, ddd, $J = 7.9, 1.3, 0.8$ Hz, H-7), and 6.726, 6.729 (0.5H, br s, H-4); and signals based on the two 4-(dimethylamino)phenyl groups: δ 2.90, 2.97 (6H each, s, $(CH_3)_2N$-4′,4″), 6.57, 6.77 (2H each, dd, $J = 8.5, 2.5$ Hz, H-2′,6′,2″,6″), and 7.27, 7.47 (2H each, dd, $J = 8.5, 2.5$ Hz, H-3′,5′,3″,5″).

Compound **18b**: ^1H NMR (THF-d_8): δ 1.18, 1.23 (3H each, d, $J = 6.8$ Hz, $(CH_3)_2CH$-8), 2.36 (3H, br s, Me-10), 2.42 (3H, br s, Me-5), 2.56 (1H, sept d, $J = 6.8, 0.7$ Hz, $(CH_3)_2CH$-8), 4.13 (1H, d, $J = 8.0$ Hz, H-6), 4.26 (1H, br q, H-10a), 4.74 (1H, d, $J = 1.4$ Hz, H-9), 6.37 (1H, ddd, $J = 8.0, 1.4, 0.7$ Hz, H-7), and 6.893, 6.897 (0.5H, br s, H-4); and signals based on the two 4-(di-



8 **9**

Figure 1. The reaction of **1** with **8** in methanol in the presence of hydrochloric acid at 60 °C for 3 h.

methylamino)phenyl groups: δ 2.87, 2.97 (6H each, s, $(CH_3)_2N$-4′,4″), 6.51, 6.78 (2H each, dd, $J = 8.5$, 2.5 Hz, H-2′,6′,2″,6″), and 7.32, 7.62 (2H each, dd, $J = 8.5$, 2.5 Hz, H-3′,5′,3″,5″).

Reaction of (*E*)-2-[4-(Dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene (13) with Tetracyanoethylene (TCNE). To a solution of (*E*)-2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene (**13**) (10 mg, 29 µmol) in benzene (1.5 mL) was added a solution of TCNE (8 mg, 63 µmol) in benzene (1.5 mL) under argon, turning the dark-green solution into a black solution, rapidly. The mixture was stirred at 25 °C for 24 h under argon, gradually giving a white precipitate of **19** and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with benzene and hexane, and was recrystallized from ethyl acetate–hexane (1:5, vol/vol) to provide pure **19** (7 mg, 12 µmol, 41% yield) as stable crystals.

Compound **19**: Colorless plates [$R_f = 0.34$ on silica-gel TLC (solv. hexane:ethyl acetate = 7:3, vol/vol)]; mp >135 °C [decomp., determined by thermal analysis (TGA and DTA)]; UV–vis λ_{max} (ethyl acetate) nm (log ε): 276 (4.47); IR ν_{max} (KBr) cm^{-1}: 2253 and 2249 (C≡N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 600.2614; calcd for $C_{37}H_{30}N_9$: $[M+H]^+$, m/z 600.2625; ^1H NMR (THF-d_8): δ 1.164, 1.168 (3H each, d, $J = 7.0$ Hz, $(CH_3)_2CH$-8), 2.29 (3H, br s, Me-5), 2.43 (3H, br s, Me-10), 2.62 (1H, sept d, $J = 7.0$, 1.0 Hz, $(CH_3)_2CH$-8), 4.10 (1H, d, $J = 7.9$ Hz, H-6), 4.44 (1H, br q, H-10a), 4.69 (1H, d, $J = 1.4$ Hz, H-9), 4.891, 4.897 (0.5H each, br d, $J = 2.6$ Hz, H-3), 6.434 (1H, ddd, $J = 7.9$, 1.4, 1.0 Hz, H-7), and 7.066, 7.071 (0.5H each, br d, $J = 2.6$ Hz, H-4); and signals based on the 4-(dimethylamino)phenyl group: δ 2.97 (6H, s, $(CH_3)_2N$-4′), 6.73 (2H, dd, $J = 8.5$, 2.5 Hz, H-2′,6′), and 7.27 (2H, dd, $J = 8.5$, 2.5 Hz, H-3′,5′).

X-ray Crystal Structure of 1,1,2,2,11,11,12,12-Octacyano-3-[4-(dimethylamino)phenyl]-8-isopropyl-5,10-dimethyl-1,2,3,6,-9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (19). A total of 9431 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 198 K. The structure was solved by direct methods (SIR92[18]) and expanded using Fourier techniques (DIRDIF94[19]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package.[20] Deposition number CCDC-622803 for compound No. 19.

Crystallographic data for **19**: $C_{41}H_{37}O_2N_9$ ($C_{37}H_{29}N_9$ + $CH_3COOC_2H_5$, FW: 687.80), colorless prism (the crystal size, $0.30 \times 0.20 \times 0.50$ mm^3), monoclinic, $P2_1/a$ (#14), $a =$ 12.865(8) Å, $b = 23.45(1)$ Å, $c = 13.219(9)$ Å, $\beta = 105.67(5)°$, $V = 3839(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.190$ g cm^{-3}, μ(Mo Kα) = 0.77 cm^{-1}, scan width: $(1.37 + 0.30 \tan\theta)°$, scan mode: ω–2θ, scan rate: 16.0° min^{-1}, measured reflections: 9431, observed reflections: 6778, No. of parameters: 469, $R1 = 0.055$, $wR2 =$ 0.163, and goodness of fit indicator: 1.22.

Results and Discussion

Preparation and Spectroscopic Properties of 9 Compared with Those of 4. In 2004 we reported that the reaction of **1** with 1,2-bis(4-methoxyphenyl)-1,2-ethanediol in methanol in the presence of hydrochloric acid at 60 °C for 3 h gave **4**, in 97% yield, via pinacol rearrangement. The reaction of **1** with 1-[4-(dimethylamino)phenyl]-2-phenyl-1,2-ethanediol under the same reaction conditions as the above however afforded numerous products and an only compound **6**, without pinacol rearrangement, could be isolated in 17% yield. A plausible reaction pathway for the formation of **4** and **6** was submitted.[8] For comparative purposes, the reaction of **1** with **8** under the same reaction conditions as the above was carried out as shown in Figure 1, yielding a new **4** analogue **9** in 81% yield, via pinacol rearrangement. Therefore, an apparent difference between the reactions of **1** with 1-[4-(dimethylamino)-phenyl]-2-phenyl-1,2-ethanediol and 1,2-bis[4-(dimethylamino)phenyl]-1,2-ethanediol (**8**) was observed. The molecular structure of **9** was established on the basis of elemental analysis and spectroscopic data [UV–vis, IR, exact FAB-MS, and ^1H and ^{13}C NMR including NOE and 2D NMR (i.e., H–H COSY, HMQC, and HMBC)].

Compound **9** was obtained as dark-green plates. The spectroscopic properties of **9** compared with those of **4**, possessing a similar framework, are described as follows (Tables 1–3). The UV–vis spectrum of **9** resembled that of **4**, while the longest absorption wavelength of **9** revealed a slight bathochromic shift (Δ 12 nm) and a slight hyperchromic effect ($\Delta \log \varepsilon =$ 0.15). These visible data corresponded to the Δ π-HOMO − π-LUMO/eV levels[27,28] of **4** and **9** (Table 1). The IR spectrum showed specific bands resulting from the C–N, aromatic C=C, and C–H bonds. The molecular formula $C_{33}H_{38}N_2$ was determined by exact FAB-MS. Elemental analysis confirmed the molecular formula $C_{33}H_{38}N_2$. The ^1H NMR spectrum showed signals consistent with a 3-guaiazulenyl group, signals consistent with two non-equivalent 4-(dimethylamino)phenyl groups, and a signal based on an ethylene group (>C=CH–), the signals of which were carefully assigned using NOE and H–H COSY techniques and computer-assisted simulation

Table 1. Comparative Studies on the Longest Wavelength Absorption Maxima, the Energy Levels,[27,28] and the Redox Potentials[a)] of **4**, **5**, **9**, and **13**

Compound	$\lambda_{\max}$/nm ($\log \varepsilon$)	π-HOMO/eV	π-LUMO/eV	Δ π-HOMO $-$ π-LUMO/eV	$E^1{}_{\text{ox}}$/V	$E^1{}_{\text{red}}$/V
4	635 (2.54)	−7.714	−1.155	−6.559	0.52	−1.73
5	661 (3.13)	−7.372	−1.090	−6.282	0.20	−1.71
9	647 (2.69)	−7.417	−0.916	−6.501	0.32	−1.75
13	654 (2.80)	−7.464	−1.032	−6.432	0.33	−1.68

a) CV data.

Table 2. Comparative Studies on Selected ^{1}H NMR Spectra (δ, ppm) of the 3-Guaiazulenyl[a)] and Vinyl Groups of **4**, **5**, **9**, and **13**

Compound	Azulenyl group				Vinyl group
	H-2	H-5	H-6	H-8	C=C*H*–Gu^3
4	7.44	6.63	7.02	7.91	7.77
5	8.14	6.56	6.99	7.97	8.12
9	7.60	6.59	7.00	7.88	7.81
13	8.01	6.56	7.00	7.97	8.10

a) Gu^3: 3-guaiazulenyl group.

Table 3. Comparative Studies on Selected ^{13}C NMR Spectra (δ, ppm) of the 3-Guaiazulenyl[a)] and Vinyl Groups of **4**, **5**, **9**, and **13**

Compound	Azulenyl group				Vinyl group
	C-2	C-5	C-6	C-8	C=*C*H–Gu^3
4	140.4	126.5	134.6	133.2	125.6
5	136.1	126.8	134.6	133.2	125.2
9	140.8	126.0	134.3	132.8	125.4
13	136.7	126.9	134.6	133.4	123.0

a) Gu^3: 3-guaiazulenyl group.

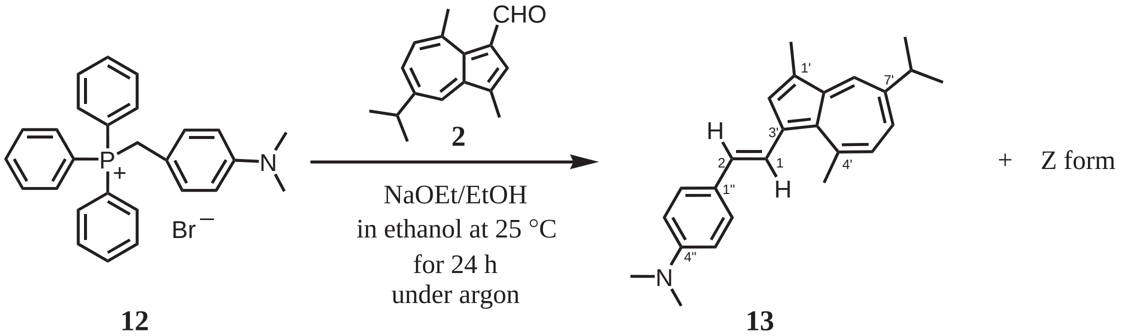
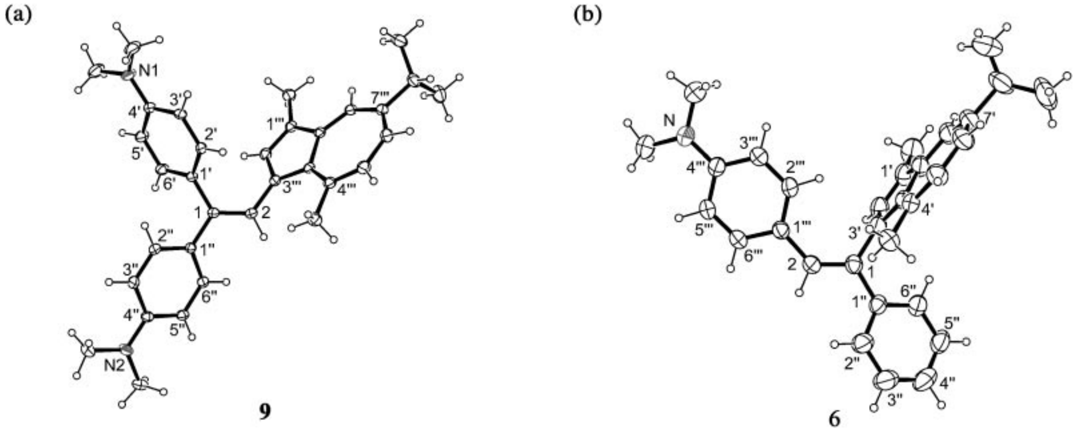


Figure 2. The Wittig reaction of **2** with **12** in ethanol in the presence of sodium ethoxide at 25 °C for 24 h under argon.

based on first-order analysis. Although the H-2‴ proton signal of **9** showed an apparent down-field shift as a result of steric hindrance and repulsion between the H-2‴ hydrogen atom and the (*Z*)-4-(dimethylamino)phenyl group along with influence from the ring current of the (*Z*)-4-(dimethylamino)phenyl group, the signals (H-5‴, H-6‴, H-8‴, and >C=CH–) of **9** coincided with those of **4** (Table 2). The ^{13}C NMR spectrum exhibited 26 carbon signals assigned by HMQC and HMBC techniques. The carbon signals (C-2‴, C-5‴, C-6‴, C-8‴, and >C=*C*H–) of **9** coincided with those of **4** (Table 3). Thus, the spectroscopic data for **9** led to the molecular structure 1,1-bis[4-(dimethylamino)phenyl]-2-(3-guaiazulenyl)ethylene. Comparing the chemical shifts for the proton and carbon signals and the UV–vis spectrum of **9** to those of **4** and **1**,[29] it can be inferred that the azulene ring of **9** twists from the plane of the >C=CH– structure as a result of steric hindrance and repulsion between the 3-guaiazulenyl and (*Z*)-4-(dimethylamino)phenyl groups. A similar reaction pathway to that of **4**[8] can be inferred for the formation of **9**.

Preparation and Spectroscopic Properties of 13 Compared with Those of 9 and 5. We reported preparation and spectroscopic properties of the (*Z*)-4-(dimethylamino)phenyl-substituted compound **6**[8] and the 1,1-bis[4-(dimethylamino)phenyl]-substituted compound **9**. For comparative purposes, the (*E*)-4-(dimethylamino)phenyl-substituted compound **13** was prepared in 12% yield, using the Wittig reaction as shown in Figure 2. The molecular structure was established on the basis of analysis similar to that of **9**. Although the presumed Z isomer[30] of **13** was observed by silica gel TLC of the reaction mixture, it could not be isolated using silica gel column chromatography and recrystallization.

Compound **13** was obtained as dark-green plates. The spectroscopic properties of **13**, compared with those of **9** and **5**,[8] are as follows (Tables 1–3). The UV–vis spectrum of **13** resembled those of **9** and **5**, while the longest absorption wavelength revealed a slight bathochromic shift (Δ 7 nm) and a slight hyperchromic effect ($\Delta \log \varepsilon = 0.11$) in comparison with that of **9**, and revealed a slight hypsochromic shift (Δ 7 nm) and a hypochromic effect ($\Delta \log \varepsilon = 0.33$) in comparison with that of **5**. These visible data correspond to the Δ π-HOMO $-$ π-LUMO/eV levels[27,28] of **5**, **9**, and **13** (Table 1). The IR spectrum showed specific bands from the C–N, aromatic C=C, and C–H bonds, whose wavenumbers coincided with those of **9**, and the –HC=CH– bonds, whose wavenumbers coincided with those of **5**. The molecular formula $C_{25}H_{29}N$ was determined by exact FAB-MS. Elemen-



9

6

Figure 3. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **9** and **6**.

Table 4. Selected C–C Bond Lengths (Å) for the 3-Guaiazulenylethylene Moieties of **4**–**6**, **9**, and **13**$^{a)}$

Atom	4	5	6	9	13
C1–C2	1.343(4)	1.32(1)	1.347(4)	1.348(3)	1.328(4)
C2–C3′	1.464(4)	1.444(8)	1.489(4)	1.468(3)	1.457(4)
C1′–C2′	1.382(5)	1.378(8)	1.373(4)	1.370(3)	1.374(4)
C2′–C3′	1.407(5)	1.452(8)	1.420(4)	1.420(3)	1.418(4)
C3′–C3a′	1.416(5)	1.391(7)	1.404(4)	1.413(3)	1.408(4)
C3a′–C4′	1.393(4)	1.404(8)	1.410(4)	1.409(3)	1.412(4)
C4′–C5′	1.390(5)	1.369(9)	1.382(4)	1.393(3)	1.381(5)
C5′–C6′	1.388(5)	1.40(1)	1.399(4)	1.402(3)	1.403(5)
C6′–C7′	1.383(4)	1.362(10)	1.386(5)	1.381(3)	1.372(5)
C7′–C8′	1.384(5)	1.397(9)	1.384(4)	1.408(3)	1.398(4)
C8′–C8a′	1.382(4)	1.351(8)	1.394(4)	1.376(3)	1.379(4)
C8a′–C1′	1.413(5)	1.388(8)	1.397(4)	1.423(3)	1.421(4)
C3a′–C8a′	1.515(4)	1.533(8)	1.502(4)	1.503(3)	1.503(4)

a) For comparative purposes, the numbering schemes for the 3-guaiazulenylethylene moieties of **4**–**6**, **9**, and **13** (see Figure 3 and Figure 4) were changed as shown in Table 4.

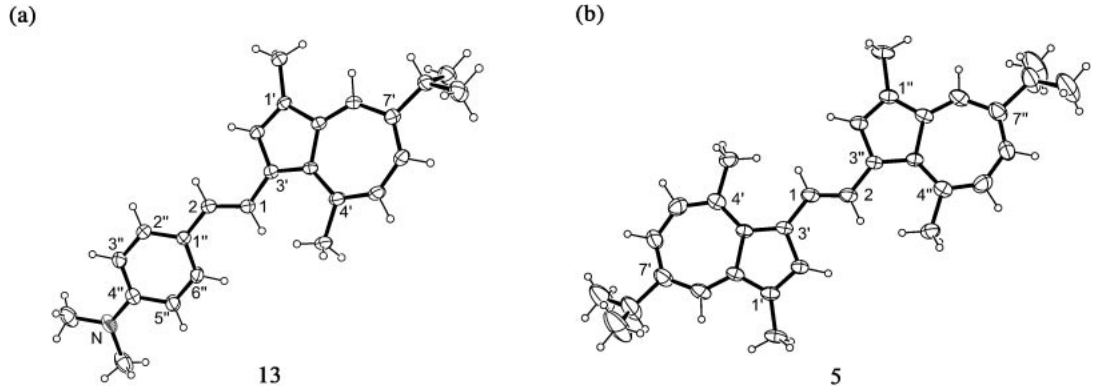
Table 5. Selected C–C and C–N Bond Lengths (Å) for the 4-(Dimethylamino)phenyl Groups of **6**, **9**, **13**, and **15**$^{a)}$

Atom	6	9		13	15
C1–C1′	1.463(4)	1.495(3)$^{b)}$	1.487(3)$^{c)}$	1.458(4)	1.448(4)
C1′–C2′	1.395(4)	1.391(3)$^{b)}$	1.401(3)$^{c)}$	1.391(4)	1.394(3)
C2′–C3′	1.372(4)	1.390(3)$^{b)}$	1.376(3)$^{c)}$	1.379(5)	1.366(4)
C3′–C4′	1.389(4)	1.400(3)$^{b)}$	1.406(3)$^{c)}$	1.382(5)	1.410(3)
C4′–C5′	1.394(4)	1.409(3)$^{b)}$	1.396(3)$^{c)}$	1.408(5)	1.411(3)
C5′–C6′	1.364(4)	1.386(3)$^{b)}$	1.385(3)$^{c)}$	1.371(5)	1.368(4)
C6′–C1′	1.392(4)	1.385(3)$^{b)}$	1.403(3)$^{c)}$	1.389(5)	1.399(3)
C4′–N′	1.382(3)	1.384(3)$^{b)}$	1.378(3)$^{c)}$	1.375(4)	1.360(3)

a) For comparative purposes, the numbering schemes for the 4-(dimethylamino)phenyl groups of **6** and **13** (see Figure 3 and Figure 4) were changed as shown in Table 5. b) 4′-(Dimethylamino)phenyl group. c) 4″-(Dimethylamino)phenyl group (see Figure 3).

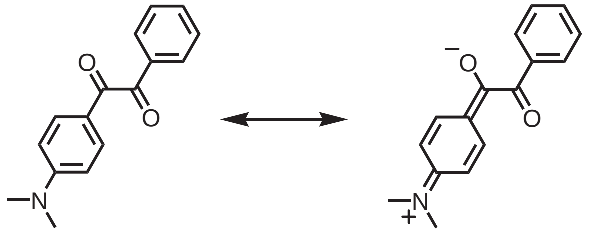
tal analysis confirmed the molecular formula $C_{25}H_{29}N$. The ^{1}H NMR spectrum showed signals from 3-guaiazulenyl and 4-(dimethylamino)phenyl groups and signals from a *trans*-HC=CH– moiety, the signals of which were carefully assigned using similar techniques to those used for **9**. Although the proton signals [H-2′ and –HC=C*H*–Gu^3 (Gu^3: 3-guaiazulenyl)] of **13** showed apparent down-field shift in comparison with the signals (H-2‴ and >C=CH–Gu^3) of **9**, the signals (H-5′, H-6′, and H-8′) of **13** coincided with the signals (H-5‴, H-6‴, and H-8‴) of **9**, and although the H-2′ signal of **13** showed an apparent up-field shift in comparison with that of **5**, the signals (H-5′, H-6′, H-8′, and –HC=C*H*–Gu^3) of **13** coincided with those of **5** (Table 2). The ^{13}C NMR spectrum exhibited 20 carbon signals assigned using similar techniques to those used for **9**. Although the carbon signals (C-2′ and –HC=*C*H–Gu^3) of **13** showed apparent up-field shifts in comparison to the signals (C-2‴ and >C=*C*H–) of **9**, the signals (C-5′, C-6′, and C-8′) of **13** coincided with the signals (C-5‴, C-6‴, and C-8‴) of **9**. The –HC=*C*H–Gu^3 signal of **13** showed an apparent up-field shift in comparison with the –HC=CH– signal of **5**, however the signals (C-2′, C-5′, C-6′, and C-8′) of **13** coincided with those of **5** (Table 3). From the spectroscopic data for **13** the molecular structure (*E*)-2-[4-(dimethylamino)phenyl]-1-(3-guaiazulenyl)ethylene was deduced.

X-ray Crystal Structure of 9 Compared with Those of 4 and 6. The recrystallization of **9** from a mixed solvent of dichloromethane and hexane (1:5, vol/vol) provided stable single crystals suitable for X-ray crystallographic analysis. The crystal structure of **9** was then determined by means of X-ray diffraction, producing accurate structural parameters. The ORTEP drawing of **9** with a numbering scheme is shown in Figure 3a along with selected bond lengths (Tables 4 and 5). The structural parameters of **9** revealed that the C–C bond length between the >C=CH– group of **9** coincided with those of **4**[8] and **6**[8] and the C1–C1′, C1–C1″, and C2–C3‴ bond lengths of **9** coincided with those of **4**. Similar to **4** and **6** (Figure 3b), the aromatic rings of the two 4′- and 4″-(dimethylamino)phenyl and 3‴-guaiazulenyl groups of **9** twisted by 49, 30, and 66° from the >C=CH– plane as a result of large steric hindrance and repulsion between the rings. The average C–C bond lengths for the seven- and five-membered rings of the 3-guaiazulenyl group (1.410 and 1.426 Å) coincided with those of **4** (1.405 and 1.427 Å) and **6** (1.409 and 1.420 Å). Thus, the crystal structure of **9** supported the molecular structure established on the basis of spectroscopic data.



13 5

Figure 4. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **13** and **5**.

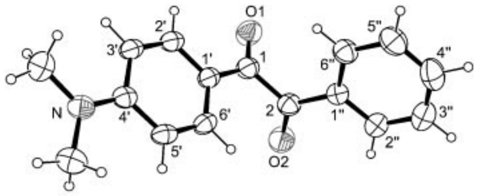


15 **15′**

Chart 3.

X-ray Crystal Structure of 13 Compared with Those of 5 and 9. Recrystallization of **13** from ethanol provided stable single crystals suitable for X-ray crystallographic analysis. The ORTEP drawing of **13** is shown in Figure 4a along with selected bond lengths (Tables 4 and 5). The structural parameters of **13** revealed that the C–C bond length of the *trans*-HC=CH– moiety of **13** coincided with that of **5**,[8] however the bond length was shorter than the >C=CH– of **9**. Although the C1–C3′ and C2–C1″ bond lengths of **13** were longer than the C1–C3′ bond length of **5**, they were shorter than the C2–C3‴ and C1–C1″ bond lengths of **9**. The crystal structure of **5** was planar (Figure 4b), however the aromatic rings of the 4″-(dimethylamino)phenyl and 3′-guaiazulenyl groups twisted by 1 and 23° from the plane of the *trans*-HC=CH– group, presumably due to the influence of inter-molecular stacking, and the average C–C bond lengths for the seven- and five-membered rings of the 3-guaiazulenyl group of **13** (1.407 and 1.425 Å) coincided with those of **5** (1.403 and 1.429 Å) and **9**. As with **9**, the crystal structure of **13** supported the molecular structure established on the basis of spectroscopic data.

X-ray Crystal Structure of 15 Compared with Those of 6, 9, and 13. In 2003 we reported the unique crystal structure of [4-(dimethylamino)phenyl]-3-guaiazulenylmethylium tetrafluoroborate with two representative resonance forms of the 3-guaiazulenylium and quinoid structures.[5] In relation to this study, our interest has been focused on the crystal structures of **6**, **9**, and **13**, with resonance forms of similar quinoid structures to the above, due to the influence of a dipole between the 4-(dimethylamino)phenylethylene group, which serves as a strong electron donor,[8] and the 3-guaiazulenyl group, which serves as both an electron acceptor and a strong electron donor.[8] Studies of the crystal structures of **6**, **9**, and **13**, compared with that of **15**, probably possessing contribution of intra-molecular charge-separated structure **15′** with a quinoid structure (Chart 3), are noteworthy. Recrystallization of **15** from ethanol was carried out, providing stable single crystals suitable for X-ray crystallographic analysis. The crystal structure of **15** was determined by means of X-ray diffraction, producing accurate structural parameters, the results of which enabled comparison with those of **6**, **9**, and **13** (Table 5). An ORTEP drawing of **15** is shown in Figure 5 together with selected bond lengths. The structural parameters of **15** reveal that the plane of the 4-(dimethylamino)phenyl ketone is twisted by 104° from that of the phenyl ketone, owing to the influence of non-bonded lone pair–lone pair repulsions in the α-diketones[31] and that the bond lengths and their alternation pattern observed for the 4-(dimethylamino)phenyl ketone, compared with those observed for the phenyl ketone, indicate an apparent contribution of **15′**. It was found that the bond lengths observed for the 4-(dimethylamino)phenyl groups of **6**, **9**, and **13** did not completely coincide with those of **15**, while their bond alternation pattern did, suggesting a small contribution of the quinoid form.



15

Figure 5. The ORTEP drawing with the numbering scheme (30% probability thermal ellipsoids) of **15**. The bond lengths (Å) of **15** are as follows: C1–C2; 1.526(4), C1–O1; 1.231(3), C1–C1′; 1.448(4), C1′–C2′; 1.394(3), C2′–C3′; 1.366(4), C3′–C4′; 1.410(3), C4′–C5′; 1.411(3), C5′–C6′; 1.368(4), C6′–C1′; 1.399(3), C4′–N; 1.360(3), N–C7′; 1.437(4), N–C8′; 1.444(3), C2–O2; 1.218(3), C2–C1″; 1.473(4), C1″–C2″; 1.379(3), C2″–C3″; 1.372(4), C3″–C4″; 1.371(5), C4″–C5″; 1.372(5), C5″–C6″; 1.383(4), and C6″–C1″; 1.385(4).

Electrochemical Properties of 9 and 13 Compared with Those of 6 and 5. The electrochemical properties of **9** were measured by means of CV and DPV [Potential (in volts) vs. SCE] in CH_3CN containing 0.1 M [n-Bu$_4$N]BF$_4$ as a support-

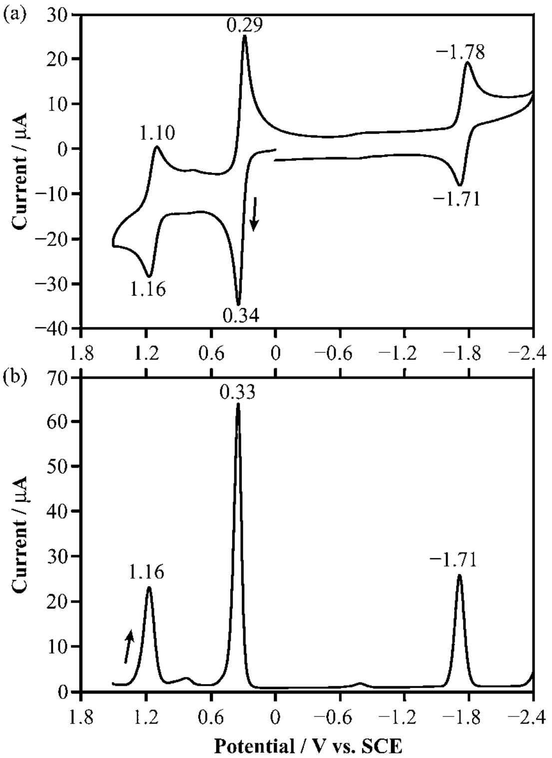


Figure 6. Cyclic (a) and differential pulse (b) voltammograms of **9** (3.0 mg, 6.5 μmol) in 0.1 M [n-Bu_4N]BF_4, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.45 (E_p) V by DPV and +0.42 ($E_{1/2}$) V by CV under the same electrochemical measurement conditions as for **9**.

ing electrolyte. Three redox potentials observed by DPV were positioned at +1.16, +0.33, and −1.71 V, and the corresponding three reversible redox potentials determined by CV were +1.13, +0.32, and −1.75 V ($E_{1/2}$ each) as shown in Figure 6. It was found that the reduction potential of **9** coincided with that of **6** and that as with **6**, underwent two-electron oxidation, however **9** was more susceptible to two-electron oxidation than **6** (Figure 7)[8] and the generated dication further underwent one-electron oxidation. On the other hand, in 1996 Nozoe et al. reported that 3,3′-biguaiazulene underwent stepwise two-electron oxidation at +0.40 V (E_1^{ox}) and +0.54 V (E_2^{ox}) by CV, generating a dication species via a cation-radical.[32] In relation to this study, in 2002 Ito et al. reported that 1,1′-biazulene underwent stepwise two-electron oxidation and reduction at +0.30 V (E_1^{ox}), +0.62 V (E_2^{ox}), −1.88 V (E_1^{red}), and −2.16 V (E_2^{red}) by CV, generating a dication species via a cation-radical and a dianion via an anion-radical.[33] Thus, a plausible electron-transfer mechanism of **9** based on its CV and DPV data can be inferred as illustrated in Scheme 1. Namely, **9** undergoes two-electron oxidation at +0.32 V by CV (+0.33 V by DPV), generating an electrochemically stable dication **9b**, occurring between the (Z)-4-(dimethylamino)phenyl and 3-guaiazulenyl groups via cation-radical **9a** and resonance form **9a′**, and further, the (E)-4-(dimethylamino)phenyl group of **9b** is oxidized to the cation-radical at a potential of +1.13 V by CV (+1.16 V by DPV), generating an electrochemically stable trication-radical **9c**. Along with the oxidation potentials, **9** is reduced to the anion-radical **9d** at a potential of −1.75 V by CV (−1.71 V by DPV).

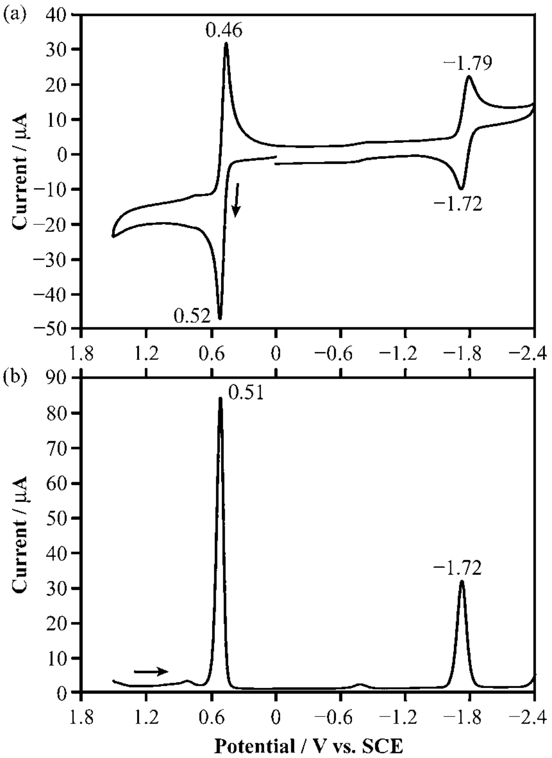
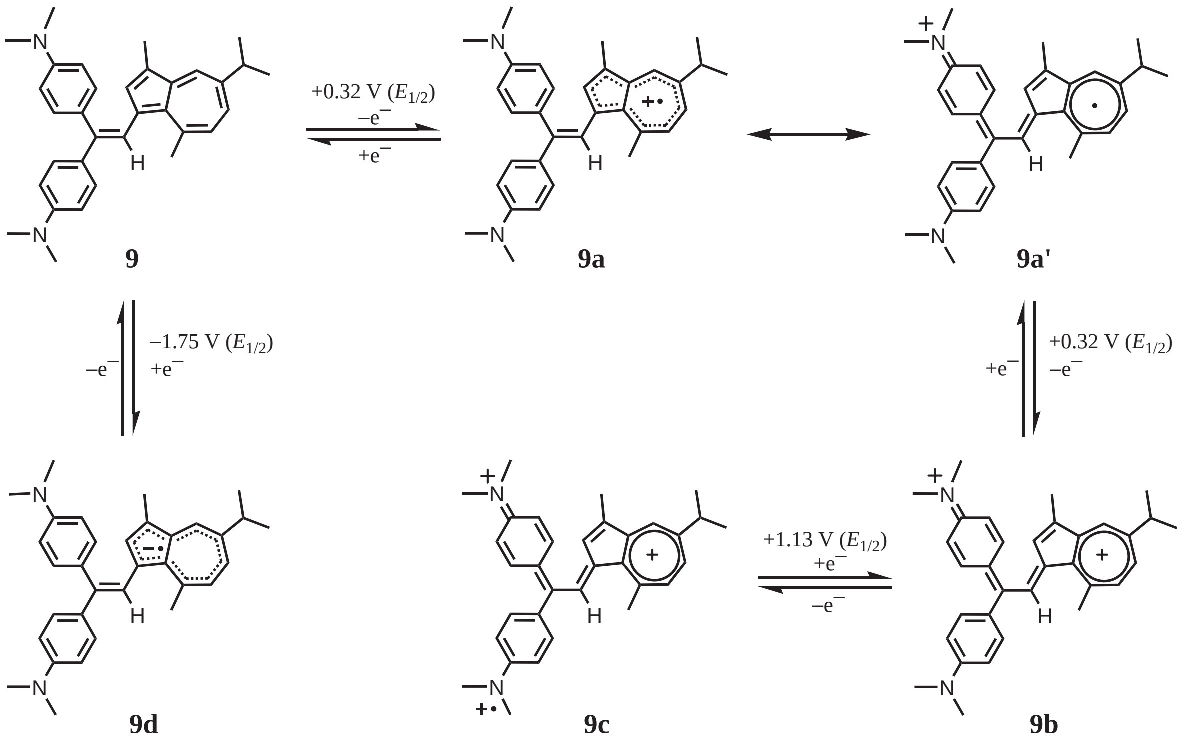


Figure 7. Cyclic (a) and differential pulse (b) voltammograms of **6** (3.0 mg, 7.1 μmol) under the same electrochemical measurement conditions as for **9**.

For comparative purposes, the electrochemical properties of **13** were measured under the same conditions as for **9**. Three redox potentials observed by DPV were positioned at the E_p values of +0.49, +0.34, and −1.67 V, and the corresponding three reversible redox potentials determined by CV were located at the values of +0.46, +0.33, and −1.68 V ($E_{1/2}$ each) as shown in Figure 8. It was found that **13** was slightly more susceptible to reduction than **9**, whose potentials corresponded to the π-LUMO/eV levels[27,28] of **13** and **9** (Table 1). The reduction potential of **13** coincided with the first reduction potential (E_1^{red}) of the E form **5** (Figure 9)[8] and as in the case of **5**, **13** underwent stepwise two-electron oxidation. From the difference between the two-electron oxidation potential patterns of the Z form **6** and the E form **13**, a plausible electron-transfer mechanism for **9** via **9a**, **9a′**, and **9b**, illustrated in Scheme 1, is suggested. Although **13** was more susceptible to oxidation than **4**, **13** was less susceptible to oxidation than **5** (Figure 9)[8] and **9**, the potentials of which corresponded to the π-HOMO/eV levels[27,28] of **4**, **5**, **9**, and **13** (Table 1). Thus, a plausible electron-transfer mechanism of **13** based on CV and DPV data can be inferred as illustrated in Scheme 2. Namely, **13** undergoes stepwise two-electron oxidation at +0.33 and +0.46 V by CV (+0.34 and +0.49 V by DPV), generating an electrochemically stable dication **13b** via the cation-radical **13a**. Along with the oxidation potentials, **13** is reduced to anion-



Scheme 1. A plausible electron-transfer mechanism based on the CV and DPV data of **9**.

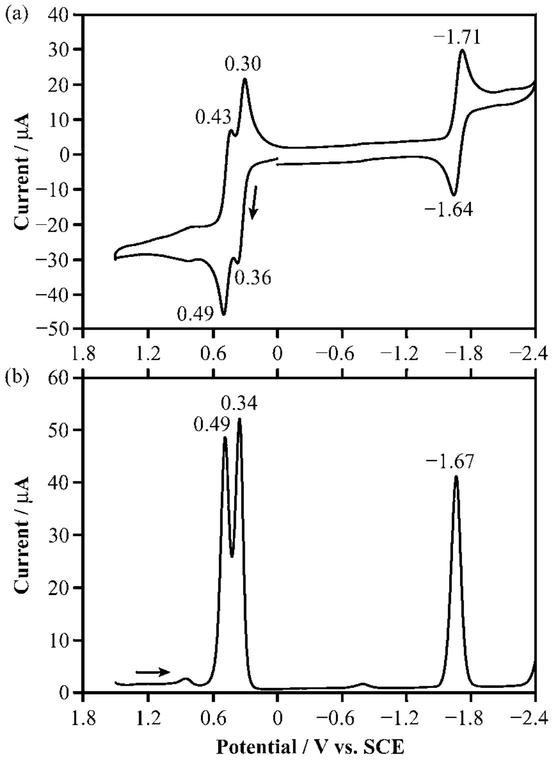


Figure 8. Cyclic (a) and differential pulse (b) voltammograms of **13** (3.0 mg, 8.7 μmol) under the same electrochemical measurement conditions as for **9**.

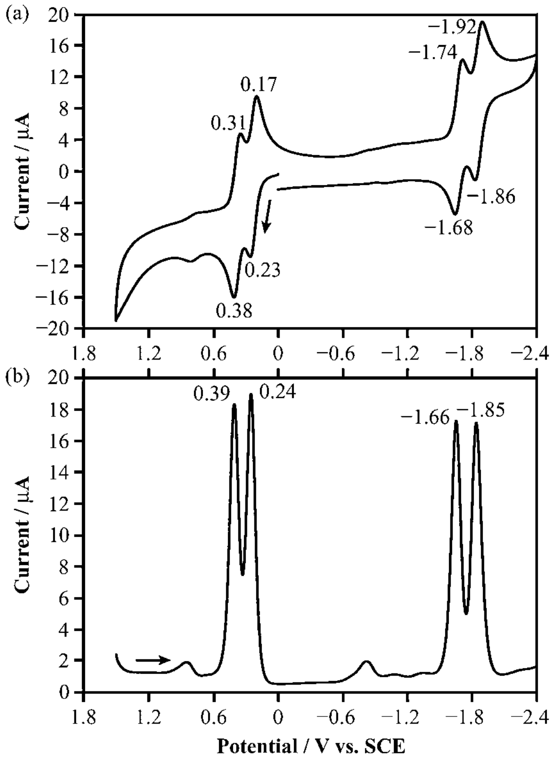
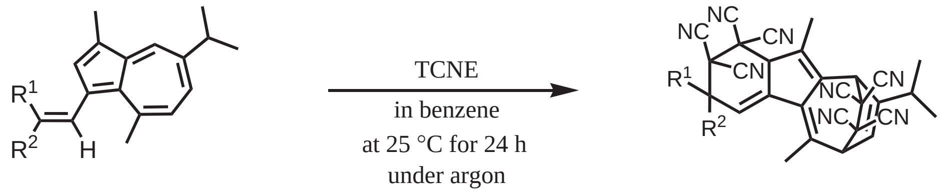


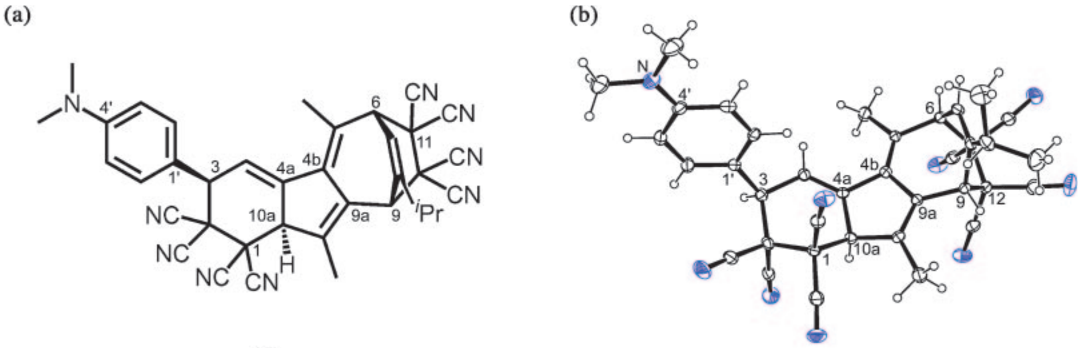
Figure 9. Cyclic (a) and differential pulse (b) voltammograms of **5** (3.0 mg, 7.1 μmol) under the same electrochemical measurement conditions as for **9**.



9: $R^1 = R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$
13: $R^1 = H, R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$

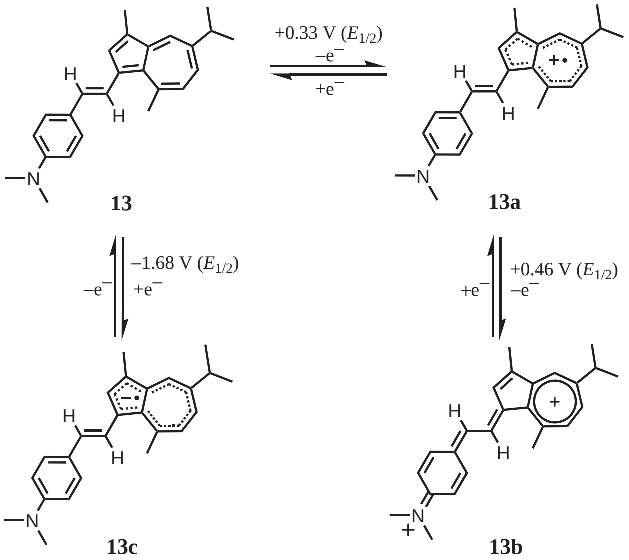
18: $R^1 = R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$
19: $R^1 = H, R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$

Figure 10. The reaction of **9** (or **13**) with 2 equiv of TCNE in benzene at 25 °C for 24 h under argon.



19

Figure 11. The molecular structure of **19** and its ORTEP drawing with the numbering scheme (30% probability thermal ellipsoids).



Scheme 2. A plausible electron-transfer mechanism based on the CV and DPV data of **13**.

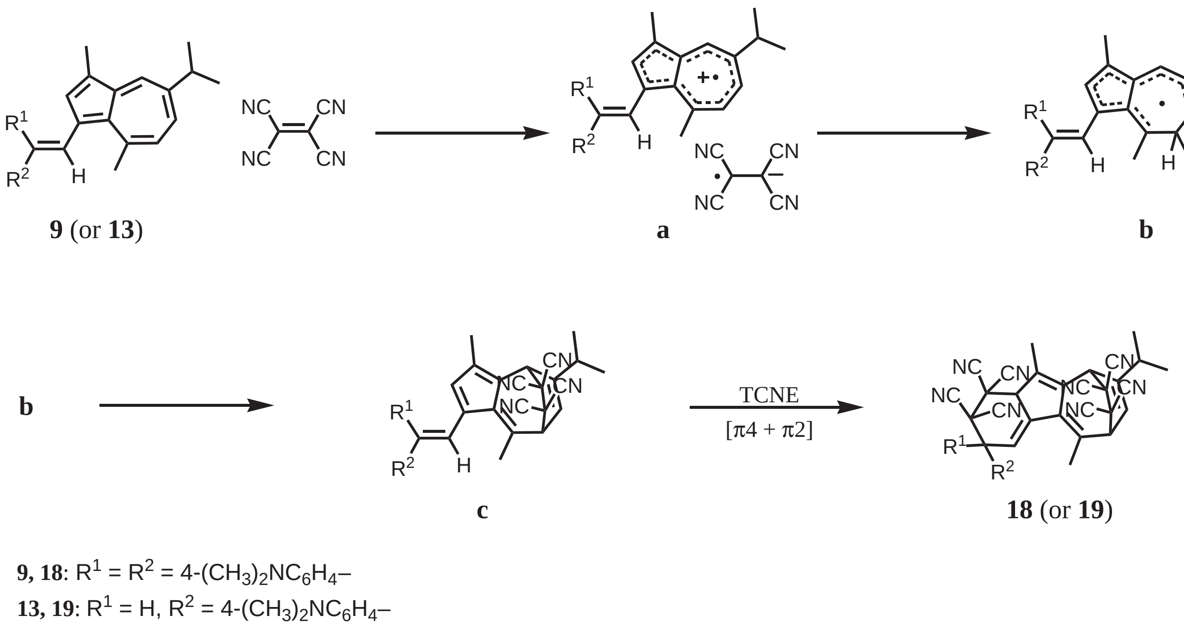
radical **13c** at a potential of −1.68 V by CV (−1.67 V by DPV). In conclusion, the redox potentials of **9** and **13** indicate that both of them serve as strong two-electron donors and one-electron acceptors.

Reaction of 9 with TCNE. For comparative purposes, the reaction of **9** with TCNE was carried out under the same reaction conditions as for **4**[12] (Figure 10), giving a new **17** analogue **18** in 74% yield, whose molecular structure was established on the basis of spectroscopic analyses.

Compound **18** was obtained as pale-green plates. The characteristic UV–vis absorption bands of **9** were not observed and the longest visible absorption wavelength appeared at λ_{max} 390 nm ($\log \varepsilon = 4.11$). The IR spectrum showed two specific bands corresponding to the –C≡N group, whose wavenumbers coincided with those of **16**[12] and **17**.[12] The protonated molecular formula $C_{45}H_{39}N_{10}$ was determined by exact FAB-MS. The ^{1}H NMR spectrum showed signals consistent with 8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydrobenz[*a*]azulene possessing two 4-(dimethylamino)phenyl groups at the C-3 position, the signals of which were carefully assigned using conventional methodology. Careful study of the ^{1}H NMR signals suggested a ca. 7:5, mixture of chromatographically inseparable diastereomers. Comparative studies of detailed spectroscopic data indicated a similar structure to that of **17**, 1,1,2,2,11,11,12,12-octacyano-3,3-bis[4-(dimethylamino)phenyl]-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene.

Reaction of 13 with TCNE. For comparative purposes, the reaction of **13** with TCNE was carried out under the same reaction conditions as for **5**[12] (Figure 10), affording a new **16** analogue **19** in 41% yield, the molecular structure of which was established on the basis of spectroscopic analyses.

Compound **19** was obtained as colorless plates. The characteristic UV–vis absorption bands of **13** were not observed and the longest UV absorption wavelength appeared at λ_{max} 276 nm ($\log \varepsilon = 4.47$). The IR spectrum showed two specific bands from the –C≡N group, whose wavenumbers coincided with those of **16**–**18**. The protonated molecular formula $C_{37}H_{30}N_9$ was determined by exact FAB-MS. The ^{1}H NMR spectrum showed signals consistent with 8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydrobenz[*a*]azulene possessing a 4-(dimethylamino)phenyl group at the C-3 position, whose signals were carefully assigned using conventional methodology. Comparative studies of detailed spectroscopic data suggested a



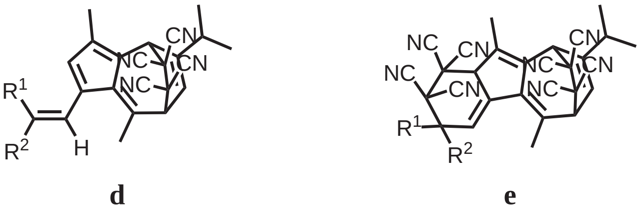
9, 18: $R^1 = R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$
13, 19: $R^1 = H$, $R^2 = 4\text{-}(CH_3)_2NC_6H_4\text{–}$

Scheme 3. A plausible reaction pathway for the formation of **18** (or **19**).

structure similar to that of **16**, 1,1,2,2,11,11,12,12-octacyano-3-[4-(dimethylamino)phenyl]-8-isopropyl-5,10-dimethyl-1,2,-3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene.

Although the crystal structure of **18** has not yet been obtained because of difficulty in obtaining a single crystal suitable for analysis, recrystallization of **19** from a mixed solvent of ethyl acetate and hexane (1:5, vol/vol) provided stable single crystals suitable for that purpose. An ORTEP drawing of **19** with a numbering scheme, indicating the molecular structure illustrated in Figure 11a, is shown in Figure 11b.

A Plausible Reaction Pathway for the Formation of 18 and 19. In 2006 we suggested a plausible reaction pathway for the formation of **16** and **17**.[12] From the molecular structures of the resulting products **18** and **19**, a plausible reaction pathway for formation can be inferred as illustrated in Scheme 3. To a solution of TCNE in benzene was added a solution of **9** (or **13**) in benzene under argon, turning the dark-green solution of **9** (or **13**) into a black solution, rapidly. This suggests that reaction of **9** (or **13**) with TCNE gives the corresponding charge-transfer (CT) complex **a**. Following addition, the reaction mixture was stirred at 25 °C for 24 h under argon, gradually precipitating a white solid of **18** (or **19**). As it so happens, azulenes are insusceptible to Diels–Alder reactions. Thus, these results suggest that CT complex **a** is converted to **18** (or **19**), presumably via the biradical **b**, intermediate **c**, and $[\pi 4 + \pi 2]$ cycloaddition of **c** with TCNE. Quite recently, we found that the reaction of 2-(3-guaiazulenyl)-1,1-bis(2-thienyl)ethylene with TCNE under the same reaction conditions gave product **d** (Chart 4), similar to intermediate **c**, and further, reaction of **d** with TCNE under the same conditions as the above rapidly afforded product **e** (Chart 4), similar to **18**, presumably by $[\pi 4 + \pi 2]$ cycloaddition.[34] Therefore, a similar reaction pathway to that of **18** and **19** can be inferred for the formation of **16** and **17**.[12] Isolation, structure determination, and properties of **a** and **c** are currently under intensive investigation.



d, e: $R^1 = R^2 =$ 2-thienyl group

Chart 4.

Conclusion

We have reported the following seven points in this paper: namely, (i) the reaction of **1** with **8** in methanol in the presence of hydrochloric acid at 60 °C for 3 h gave **9** in 81% yield, via pinacol rearrangement; (ii) the Wittig reaction of **2** with **12** in ethanol containing NaOEt at 25 °C for 24 h under argon afforded **13** in 12% yield; (iii) the longest absorption wavelengths of **9** and **13** corresponded to their Δ π-HOMO − π-LUMO/eV levels; (iv) the crystal structures of **9** and **13** were determined, supporting molecular structures established on the basis of spectroscopic data; (v) the electrochemical properties of **9** and **13** showed that both serve as strong two-electron donors and one-electron acceptors, whose redox potentials corresponded to their π-HOMO and π-LUMO/eV levels and further, a plausible electron-transfer mechanism based on the redox potentials of these compounds was proposed; (vi) reaction of **9** and **13** with 2 equiv of TCNE in benzene at 25 °C for 24 h under argon gave unique products **18** and **19**, possessing interesting structures, in 74 and 41% yields and further, a plausible reaction pathway for the formation of **16**–**19** was suggested; and (vii) along with the spectroscopic properties of **18** and **19**, the crystal structure of **19** was determined.

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17 1,2-Bis[4-(dimethylamino)phenyl]-1,2-ethanediol (**8**) was prepared according to the following procedures. To a solution of NaBH$_4$ (10 mg, 264 μmol) in ethanol (1.5 mL) was added a solution of commercially available 1,2-bis[4-(dimethylamino)phenyl]-1,2-ethanedione (**7**) (50 mg, 169 μmol) in dichloromethane (1.5 mL). The mixture was stirred at 25 °C for 3 h then distilled water (10 mL) was added. The resulting product was extracted with dichloromethane (10 mL × 3), washed with distilled water, dried (MgSO$_4$), and evaporated in vacuo. The obtained residue was recrystallized from ethanol, providing pure product **8** (46 mg, 153 μmol, 91% yield) as stable crystals. Compound **8**: Colorless plates [$R_f = 0.12$ on silica gel TLC (solv. hexane:ethyl acetate: benzene = 7:2:1, vol/vol/vol)]; IR $\nu_{\max}$ (KBr) cm^{-1}: 3341 (O–H), 2955–2797 (C–H), 1612, 1516 (C=C), 1315 (C–N), and 1034 (C–O); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 301.1897; Calcd for $C_{18}H_{25}N_2O_2$: $[M + H]^+$, m/z 301.1916; The relative intensity of the ^{1}H NMR signals for **8** showed a ca. 20:1 mixture of the *meso*-**8a** and enantiomeric **8b** forms. **8a**: ^{1}H NMR (methanol-d_4): δ 1.95 (2H, br s, OH), 2.93 (6H, s, $(CH_3)_2N$-4′,4″), 4.59 (2H, s, H-1,2), 6.71 (4H, dd, $J = 7.5$, 2.5 Hz, H-3′,5′,3″,5″), and 7.19 (4H, dd, $J = 7.5$, 2.5 Hz, H-2′,6′,2″,6″); **8b**: ^{1}H NMR (methanol-d_4): δ 2.89 (6H, s, $(CH_3)_2N$-4′,4″), 6.61 (4H, dd, $J = 7.6$, 2.5 Hz, H-3′,5′,3″,5″), and 6.94 (4H, dd, $J = 7.6$, 2.5 Hz, H-2′,6′,2″,6″). The OH and H-1,2 signals of **8b** could not be observed.

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21 3-Formylguaiazulene (**2**) was prepared according to the following procedures.^{22} To a solution of commercially available guaiazulene (**1**) (100 mg, 505 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 the resulting product 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 (9:1, vol/vol). The crude product was recrystallized from hexane to provide pure **2** (108 mg, 478 μmol, 95%) as stable crystals.

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24 [4-(Dimethylamino)benzyl]triphenylphosphonium bromide (**12**) was prepared according to the following procedures.^{25} To a solution of 4-(dimethylamino)benzyl alcohol (**11**) (120 mg, 795 μmol) in chloroform (3 mL) was added a solution of triphenylphosphine hydrobromide (273 mg, 795 μmol) in chloroform (3 mL). The mixture was stirred at reflux temperature for 1 h under argon. After the reaction, diethyl ether (10 mL) was added to the reaction mixture and then centrifuged at 2.5 krpm for 1 min. The crude product was carefully washed with diethyl ether, providing pure **12** (340 mg, 714 μmol, 90% yield) as a white powder.

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27 The accurate parameters for the crystal structures of **4**, **5**, **9**, and **13** were transferred to a WinMOPAC (Ver. 3.0) program^{28} and their energy levels were calculated. A keyword (1 SCF) was used.

28 The computer program was developed by Fujitsu Ltd., Japan.

29 Guaiazulene (**1**): UV–vis $\lambda_{\max}$ (CH_3CN) 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); ^1H NMR (benzene-d_6): δ 1.22 (6H, d, $J = 7.0$ Hz, $(CH_3)_2CH$-7), 2.615 (3H, s, Me-4), 2.624 (3H, br s, Me-1), 2.83 (1H, sept, $J = 7.0$ Hz, Me_2CH-7), 6.79 (1H, d, $J = 11.0$ Hz, H-5), 7.22 (1H, dd, $J = 11.0$, 2.0 Hz, H-6), 7.31 (1H, d, $J = 4.0$ Hz, H-3), 7.69 (1H, d, $J = 4.0$ Hz, H-2), and 8.22 (1H, d, $J = 2.0$ Hz, H-8); ^{13}C NMR (benzene-d_6): δ 144.1 (C-4), 139.7 (C-7), 138.1 (C-8a), 137.2 (C-3a), 136.7 (C-2), 134.6 (C-6), 133.2 (C-8), 125.4 (C-1), 125.2 (C-5), 113.5 (C-3), 38.5 (Me_2CH-7), 24.8 ($(CH_3)_2CH$-7), 24.0 (Me-4), and 13.0 (Me-1); DPV (E_p), +0.65 and −1.77 V; CV, +0.69 V (E_{pa}) and −1.79 V ($E_{1/2}$) under the same electrochemical measurement conditions as for **9**.

30 The presumed Z isomer of **13**: Green paste [$R_f = 0.66$ on silica gel TLC (solv. hexane:ethyl acetate:benzene = 7:2:1, vol/vol/vol) under the same conditions as for **13**].

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