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]triphenyl-phosphonium 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);



Chart 1.

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(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 analysis¹² 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 ¹H and 125 MHz for ¹³C) and JNM-ECA600 (600 MHz for ¹H and 150 MHz for ¹³C) cryospectrometer at 25 °C. The ¹HNMR 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-ethanediol¹⁷ (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 (MgSO₄), 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 $[R_f = 0.48 \text{ on silica-gel TLC}]$ (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 C₃₃H₃₈N₂: C, 85.67; H, 8.28; N, 6.05%; UV–vis λ_{max} (CH₃CN) 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 ν_{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 C₃₃H₃₈N₂: M⁺, m/z462.3035; ¹HNMR (benzene- d_6): signals based on the 3-guaiazulenyl group: δ 1.73 (6H, d, J = 7.0 Hz, (CH₃)₂CH-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: & 2.45 (6H, s, (CH₃)₂N-4'), 2.54 (6H, s, $(CH_3)_2N-4''$, 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); ¹³C 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 ((CH₃)₂N-4"), 40.0 ((CH₃)₂N-4'), 37.9 (Me₂CH-7"'), 27.8 (Me-4""), 24.5 ((CH₃)₂CH-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 $2\theta_{\text{max}} = 55.0^{\circ}$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR92¹⁸) and expanded using Fourier techniques (DIRDIF94¹⁹). 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), darkgreen prism (the crystal size, $0.50 \times 0.30 \times 0.50 \text{ mm}^3$), triclinic, $P\bar{1}$ (#2), a = 10.589(2) Å, b = 15.368(2) Å, c = 8.768(1) Å, $\alpha = 95.78(1)^\circ$, $\beta = 105.56(1)^\circ$, $\gamma = 79.47(1)^\circ$, V = 1349.5(4) Å³, Z = 2, $D_{calcd} = 1.139 \text{ g cm}^{-3}$, μ (Mo K α) = 0.66 cm⁻¹, scan width: $(1.21 + 0.30 \tan \theta)^\circ$, scan mode: ω -2 θ , 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-guai-azulenyl)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 bromide²³⁻²⁵ (**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 ($20 \text{ mL} \times 3$). The extract was washed with distilled water, dried (MgSO₄), 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 $[R_f = 0.60 \text{ on silica-gel TLC}]$ (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 C₂₅H₂₉N: C, 87.41; H, 8.51; N, 4.08%; UV-vis λ_{max} (CH₃CN) nm (log ε): 228 (4.39), 246 (4.33), 287 (4.41), 333 (4.59), 421 (4.61), and 654 (2.80); IR ν_{max} (KBr) cm⁻¹: 2955–2800 (C–H), 2955, 949 (–HC=CH–), 1612, 1520 (C=C), and 1358 (C-N); exact FAB-MS (3-nitrobenzvl alcohol matrix): found: m/z 343.2298; calcd for C₂₅H₂₉N: M⁺, m/z 343.2300; ¹HNMR (benzene-d₆); signals based on the 3guaiazulenyl group: δ 1.20 (6H, d, J = 7.2 Hz, (CH₃)₂CH-7'), 2.56 (3H, s, Me-1'), 2.73 (1H, sept, J = 7.2 Hz, (CH₃)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, (CH₃)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); ¹³C 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 ((CH₃)₂N-4"), 37.9 ((CH₃)₂CH-7'), 28.4 (Me-4'), 24.5 ((CH₃)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 $2\theta_{max} = 55.0^{\circ}$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR92¹⁸) and expanded using Fourier techniques (DIRDIF94¹⁹). 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**: C₂₅H₂₉N (FW: 343.51), dark-green prism (the crystal size, $0.50 \times 0.30 \times 0.50$ mm³), monoclinic, P_{2_1}/n (#14), a = 14.545(8) Å, b = 9.325(7) Å, c = 16.495(8) Å, $\beta = 114.79(4)^{\circ}$, V = 2031(2) Å³, Z = 4, $D_{calcd} = 1.123$ g cm⁻³, μ (Mo K α) = 0.64 cm⁻¹, scan width: (1.21 + 0.30 tan θ)°, scan mode: ω -2 θ , 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-1,2ethanedione (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 C₁₆H₁₅O₂N: C, 75.87; H, 5.97; N, 5.53%; exact EI-MS, found: m/z 253.1096, calcd for C₁₆H₁₅O₂N: M⁺, 253.1143.

X-ray Crystal Structure of 1-[4-(Dimethylamino)phenyl]-2phenyl-1,2-ethanedione (15). A total of 3475 reflections with $2\theta_{\text{max}} = 55.0^{\circ}$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at 296 K. The structure was solved by direct methods (SIR97²⁶) and expanded using Fourier techniques (DIRDIF94¹⁹). 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, $0.80 \times 0.60 \times 0.20 \text{ mm}^3$), monoclinic, $P2_1/c$ (#14), a = 13.010(3) Å, b = 7.710(4) Å, c = 14.234(2) Å, $\beta = 109.14(1)^\circ$, V = 1348.9(7) Å³, Z = 4, $D_{calcd} = 1.247 \text{ g cm}^{-3}$, μ (Mo K α) = 0.82 cm⁻¹, scan width: $(1.47 + 0.30 \tan \theta)^\circ$, scan mode: $\omega - 2\theta$, scan rate: $8.0^\circ \text{min}^{-1}$, 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 μ mol) in benzene (1.5 mL) was added a solution of TCNE (11 mg, 86 μ mol) 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 μ mol, 74% yield) as stable crystals.

Compound **18**: Pale-green plates; mp 147 °C [determined by thermal analysis (TGA and DTA)]; UV–vis λ_{max} (ethyl acetate) nm (log ε): 270 (4.64), 284 (4.63), and 390 (4.11); IR ν_{max} (KBr) cm⁻¹: 2253 and 2249 (C \equiv N); exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 719.3324; calcd for C₄₅H₃₉-N₁₀: [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, (CH₃)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, (CH₃)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, (CH₃)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, (C H_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, (CH₃)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-



Figure 1. The reaction of 1 with 8 in methanol in the presence of hydrochloric acid at $60 \,^{\circ}$ C for 3 h.

methylamino)phenyl groups: δ 2.87, 2.97 (6H each, s, (CH₃)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 μ mol) in benzene (1.5 mL) was added a solution of TCNE (8 mg, 63 μ mol) 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 μ mol, 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 \mathcal{E}): 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 C₃₇H₃₀N₉: $[M + H]^+$, m/z 600.2625; ¹H NMR (THF- d_8): δ 1.164, 1.168 (3H each, d, J = 7.0 Hz, (CH₃)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, (CH₃)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 $2\theta_{max} = 55.0^{\circ}$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR92¹⁸) and expanded using Fourier techniques (DIRDIF94¹⁹). 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**: $C_{41}H_{37}O_2N_9$ ($C_{37}H_{29}N_9$ + CH₃COOC₂H₅, FW: 687.80), colorless prism (the crystal size, $0.30 \times 0.20 \times 0.50$ mm³), monoclinic, $P2_1/a$ (#14), a =

12.865(8) Å, b = 23.45(1) Å, c = 13.219(9) Å, $\beta = 105.67(5)^{\circ}$, V = 3839(3) Å³, Z = 4, $D_{calcd} = 1.190 \text{ g cm}^{-3}$, μ (Mo K α) = 0.77 cm⁻¹, scan width: $(1.37 + 0.30 \tan \theta)^{\circ}$, scan mode: $\omega - 2\theta$, 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 ¹³C 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 ($\Delta \log \mathcal{E} =$ 0.15). These visible data corresponded to the $\Delta \pi$ -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 C33H38N2 was determined by exact FAB-MS. Elemental analysis confirmed the molecular formula C₃₃H₃₈N₂. 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	$\lambda_{\max}/nm \ (\log \mathcal{E})$	π -HOMO/eV	π -LUMO/eV	$\Delta \pi$ -HOMO – π -LUMO/eV	E^{1}_{ox}/V	$E^{1}_{\rm red}/{\rm V}$
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 ¹H NMR Spectra (δ, ppm) of the 3-Guaiazulenyl^{a)} and Vinyl Groups of **4**, **5**, **9**, and **13**

C 1		Azuleny	Vinyl group		
Compound	H-2	H-5	H-6	H-8	$C = CH - Gu^3$
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

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

		Vinyl group			
Compound	C-2	C-5	C-6	C-8	$C = CH - Gu^3$
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) Gu³: 3-guaiazulenyl group.

a) Gu³: 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 ¹³C 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=CH-) 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 isomer³⁰ 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 hypeschromic 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 $\Delta \pi$ -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 C₂₅H₂₉N was determined by exact FAB-MS. Elemen-



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.

tal analysis confirmed the molecular formula C25H29N. The ¹HNMR 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=CH-Gu³ (Gu³: 3-guaiazulenyl)] of 13 showed apparent down-field shift in comparison with the signals (H-2^{'''} and >C=CH-Gu³) 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=CH-Gu³) of 13 coincided with those of 5 (Table 2). The ¹³C NMR spectrum exhibited 20 carbon signals assigned using similar techniques to those used for 9. Although the carbon signals (C-2' and $-HC=CH-Gu^3$) of 13 showed apparent up-field shifts in comparison to the signals (C-2^{'''} and >C=CH-) 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=CH–Gu³ 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-

Table 5. Selected C-C and C-N Bond Lengths (Å) for the4-(Dimethylamino)phenyl Groups of 6, 9, 13, and 15^{a)}

Atom	6	9	13	15
C1C1'	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).

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.



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



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=CHmoiety 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 tetra-fluoroborate 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



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).

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 -diketones³¹ 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.

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 CH₃CN containing 0.1 M [*n*-Bu₄N]BF₄ 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*-Bu₄N]BF₄, CH₃CN (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 $-2.16 \text{ V} (E_2^{\text{red}})$ 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



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.

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).

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 $E_{\rm p}$ 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 $-1.68 V (E_{1/2} \text{ each})$ 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 $^{2\overline{7},28}$ 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 $13 (3.0 \text{ mg}, 8.7 \mu \text{mol})$ 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 μ mol) under the same electrochemical measurement conditions as for 9.



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



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

 $\begin{array}{c} \begin{array}{c} +0.33 V(E_{1/2}) \\ -e^{-} \\ H \\ -N \\ 13 \\ -e^{-} \\ +e^{-} \\ +e^$

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 $\lambda_{\rm max}$ 390 nm (log $\mathcal{E} = 4.11$). The IR spectrum showed two specific bands corresponding to the $-C \equiv N$ group, whose wavenumbers coincided with those of 16¹² and 17.¹² The protonated molecular formula C45H39N10 was determined by exact FAB-MS. The ¹HNMR 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 ¹HNMR 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 $\mathcal{E} = 4.47$). The IR spectrum showed two specific bands from the $-C \equiv N$ 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 ¹H 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: R¹ = R² = 4-(CH₃)₂NC₆H₄-13, 19: R¹ = H, R² = 4-(CH₃)₂NC₆H₄-

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 $\Delta \pi$ -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% vields 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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1,2-Bis[4-(dimethylamino)phenyl]-1,2-ethanediol (8) was 17 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 $(10 \text{ mL} \times 3)$, washed with distilled water, dried (MgSO₄), 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 ν_{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/z301.1916; The relative intensity of the ¹HNMR signals for 8showed a ca. 20:1 mixture of the meso-8a and enantiomeric 8b forms. 8a: ¹H NMR (methanol- d_4): δ 1.95 (2H, br s, OH), 2.93

(6H, s, (CH₃)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**: ¹H NMR (methanol- d_4): δ 2.89 (6H, s, (CH₃)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 μ mol) in *N*,*N*-dimethylformamide (DMF) (3.0 mL) was added a solution of phosphoryl chloride (100 μ L). 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 (MgSO₄), 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 μ mol, 95%) as stable crystals.

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23 4-(Dimethylamino)benzyl alcohol (11) was prepared according to the following procedures. To a powder of NaBH₄ (15 mg, 396 μ mol) was added a solution of 4-(dimethylamino)benzaldehyde (10) (50 mg, 336 μ mol) in ethanol (1.5 mL). The mixture was stirred at 25 °C for 3 h. After the reaction, distilled water (10 mL) 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 (MgSO₄), and evaporated in vacuo, providing pure 11 (41 mg, 272 μ mol, 81% yield) as a pale yellow oil.

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) program²⁸ 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 λ_{max} (CH₃CN) 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, (CH₃)₂CH-7), 2.615 (3H, s, Me-4), 2.624 (3H, br s, Me-1), 2.83 (1H, sept, J = 7.0 Hz, Me₂CH-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); ¹³C 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 (Me₂CH-7), 24.8 ((CH₃)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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34 Details will be reported elsewhere.