Preparation, Crystal Structure, and Spectroscopic, Chemical, and Electrochemical Properties of (2*E*,4*E*)-1-(3-Guaiazulenyl)-4-(2-thienyl)-1,3-butadiene

Shin-ichi Takekuma,*1 Norihito Kobayashi,¹ Toshie Minematsu,² and Hideko Takekuma¹

¹Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502

²School of Pharmaceutical Sciences, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502

Received February 19, 2013; E-mail: takekuma@apch.kindai.ac.jp

Wittig reaction of (*E*)-2-(2-thienyl)ethylene-1-carbaldehyde with [(3-guaiazulenyl)methyl]triphenylphosphonium bromide in ethanol containing sodium ethoxide (=NaOC₂H₅) at 25 °C for 24 h under argon gives the two (2*E*,4*E*)- and (2*E*,4*Z*)-geometric isomers of a new compound 1-(3-guaiazulenyl)-4-(2-thienyl)-1,3-butadiene, the only title (2*E*,4*E*)-form, of which can be isolated as single crystals. Preparation, chemical and spectroscopic properties, crystal structure, and electrochemical behavior of the target (2*E*,4*E*)-form, compared with those of (*E*)-1-(3-guaiazulenyl)-2-(2-thienyl)ethylene and the structurally related new compound (3-guaiazulenyl)[(*E*)-2-(2-thienyl)ethenyl]methylium hexafluorophosphate, are documented.

In previous papers,^{1–20} we reported a facile preparation and crystal structures as well as spectroscopic, chemical, and electrochemical properties of new conjugated (and delocalized) π -electron systems possessing a 3-guaiazulenyl (=5-isopropyl-3,8-dimethylazulen-1-yl)^{1-8,10-20} [or an azulen-1-yl^{7,17} or a 3-(methoxycarbonyl)azulen-1-yl9] group. During the course of our basic and systematic investigations on naturally occurring guaiazulene (=7-isopropyl-1,4-dimethylazulene)²¹ (3) and parent azulene and its derivative, we recently found that the (E)-ethylene derivative 2E (Chart 1) serves as a stronger oneelectron donor¹⁹ and a stronger one-electron acceptor¹⁹ than the starting material 3^{22} and further, that the reactions of **2E** with tetracyanoethylene (=TCNE), which serves as a strong oneelectron acceptor, in benzene [and in N,N-dimethylformamide (=DMF)] at 25 °C for 24 h under argon give unique products 8 (and 9) (Chart 2), possessing interesting molecular structures, respectively. A reaction mechanism for the formation of 8

(and 9) was also proposed.¹⁹ In relation to our studies on a preparation and properties of 2E, for example, preparations and properties of the 2-thienyl- and aryl-substituted (E)-ethyl ene^{23-25} and (2E, 4E)-1.3-butadiene^{26,27} derivatives have been reported; however, none have really been documented for the title basic studies. Therefore, our next challenge has quite recently been focused on the following investigations: namely, (i) a preparation of the title new extended π -electron system **1E** (Chart 1) compared with that of 2E;¹⁹ (ii) the reaction behavior of 1E with TCNE in benzene (and in DMF) under the same reaction conditions as for $2E^{19}$ and a reaction mechanism for the formation of the resulting products; and (iii) the crystal structure and the characteristic properties of 1E compared with those of 2E and the structurally related new propenium ion derivative 19 with a delocalized π -electron system (Chart 3). We now wish to report the detailed basic studies on the above three points (i)-(iii) with a view to comparative study.





Chart 1. For comparative purposes on the ¹H and ¹³C NMR signals and the crystal structures of **1E** and the previously reported **2E**,¹⁹ the numbering schemes of their compounds were changed as shown in Chart 1, Figure 3, and Figure 4.





Chart 3. The structure of a new monocarbenium ion compound 19 with the two representative resonance structures of the 3-guaiazulenylium ion form 19a and the 2-thienylium ion form 19b.

Experimental

General. Melting points were taken on a Yanagimoto MP-S3 instrument. Elemental analysis of the monocarbenium ion compound **19** was taken on a Yanako MT-3 CHN corder. EI-MS and FAB-MS spectra were taken on a JEOL The Tandem Mstation JMS-700 TKM data system. IR and UV–vis spectra were taken on a Shimadzu FTIR-8300 grating spectrometer and a Beckman DU640 spectrophotometer. NMR spectra were recorded with a JNM-ECA500 (500 MHz for ¹H and 125 MHz for ¹³C) or JNM-ECA700 (700 MHz for ¹H and 176 MHz for ¹³C) cryospectrometer at 25 °C. ¹H NMR spectra were assigned using computer-assisted simulation (software: gNMR developed by Adept Scientific plc) on a DELL Dimension 9200 personal computer with a Pentium IV processor. Cyclic and differential pulse voltammograms (=CV and DPV) were measured with an ALS Model 600 electrochemical analyzer.

Preparation of (*E*)-2-(2-Thienyl)ethylene-1-carbaldehyde²⁸ (7). Preparation of 7 was according to the experimental procedures documented in Ref. 28: namely, to a mixture of vinyl acetate (0.02 mL, 216 µmol) and thiophene-2-carbaldehyde (6) (24 mg, 214 µmol) in THF (5 mL) was added slowly a stirred suspension of Ba(OH)₂ (37 mg, 216 µmol) in THF (3 mL) and further, the reaction mixture, which was refluxed for 8 h. The reaction mixture after cooling was poured into cold water and then was filtered to remove the insoluble barium salts. The filtrate was extracted with chloroform (10 mL × 3), and the obtained organic layer was washed with water, dried (MgSO₄), and concentrated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with benzene–hexane–ethyl acetate (8:8:1, vol/vol/vol) as an eluant (several times), providing pure 7 (23 mg, 167 µmol, 78% yield).

Preparation of (*2E*,*4E*)-1-(3-Guaiazulenyl)-4-(2-thienyl)-1,3-butadiene (1E). To a solution of (*E*)-2-(2-thienyl)ethylene-1-carbaldehyde²⁸ (7) (27 mg, 200 µmol) in ethanol (5 mL) was added a solution of the previously reported [(3-guaiazulenyl)methyl]triphenylphosphonium bromide^{15,16} (5) (110 mg, 200 µmol) in ethanol (5 mL) containing sodium ethoxide (27 mg, 400 µmol) under argon. The mixture was stirred at 25 °C for 24 h under argon. After the reaction, distilled-water was added to the mixture and then, the resulting products were extracted with dichloromethane (20 mL × 3). The extract was washed with distilled-water, dried (MgSO₄), and concentrated 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. An inseparable mixture of the two geometric isomers 1 (53 mg, 160 μ mol, 80% yield) thus obtained was recrystallized from ethanol–chloroform (5:1, vol/vol) (several times) to provide pure 1E (11 mg, 34 μ mol, 17% yield) as single crystals. Along with the above results, each yield of the (2*E*,4*E*)-form 1E (70%) and (2*E*,4*Z*)-1-(3-guaiazulenyl)-4-(2thienyl)-1,3-butadiene (1Z) (10%) was calculated from relative intensities for the 700 MHz ¹H NMR signals of an inseparable mixture of the two geometric isomers 1E and 1Z.

Compound 1E: Dark-green needles $[R_f = 0.63 \text{ on silica gel}]$ TLC (solv. hexane:ethyl acetate = 4:1, vol/vol)]; mp 113 °C; exact EI-MS (70 eV): found: m/z 332.1599; calcd for C₂₃H₂₄S: M⁺, m/z 332.1573; IR ν_{max}/cm^{-1} (KBr): 2954–2866 (C–H), 975 (-CH=CH-), 1581, 1542 (C=C), and 682 (C-S); UV-vis $\lambda_{\text{max}}/\text{nm}$ (log ε) in CH₂Cl₂: 227 (4.34), 251 (4.30), 258 (4.29), 290 (4.33), 345 (4.56), 437 (4.76), and 645 (2.84). Details are shown in Figure 1a: 700 MHz ¹H NMR (benzene- d_6): signals from a 3-guaiazulenyl group: δ 1.16 (6H, d, J = 6.7 Hz, (CH₃)₂CH-7"), 2.49 (3H, br s, Me-1"), 2.69 (3H, s, Me-4"), 2.69 (1H, sept, J = 6.7 Hz, (CH₃)₂CH-7"), 6.54 (1H, d, J =10.4 Hz, H-5"), 6.96 (1H, dd, J = 10.4, 2.0 Hz, H-6"), 7.89 (1H, br s, H-2"), and 7.92 (1H, d, J = 2.0 Hz, H-8"); signals from a 2-thienyl group: δ 6.73 (1H, dd, J = 4.7, 3.4 Hz, H-4'), 6.75 (1H, br d, J = 4.7 Hz, H-5'), and 6.81 (1H, br d, J =3.4 Hz, H-3'); and signals from a (2E, 4E)-1,3-butadiene unit: δ 6.69 (1H, d, J = 15.2 Hz, H-1), 6.84 (1H, br dd, J = 15.2, 10.8 Hz, H-2), 7.07 (1H, br dd, J = 15.0, 10.8 Hz, H-3), and 7.57 (1H, d, J = 15.0 Hz, H-4); 176 MHz ¹³C NMR (benzene d_6): δ 146.5 (C-4"), 144.2 (C-2'), 141.8 (C-8a"), 141.2 (C-7"), 136.3 (C-2"), 134.9 (C-6"), 133.6 (C-8"), 133.3 (C-3a"), 131.3 (C-3), 130.9 (C-4), 127.7 (C-4',5"), 127.5 (C-2), 127.2 (C-3"), 126.7 (C-1"), 125.4 (C-3'), 123.8 (C-5'), 123.3 (C-1), 37.9 ((CH₃)₂CH-7"), 28.4 (Me-4"), 24.4 ((CH₃)₂CH-7"), and 13.1 (Me-1"). For comparative purposes, the above ¹H and ¹³C NMR signals (δ) are shown in Tables 1 and 2.

Compound **1Z**: 700 MHz ¹H NMR (benzene-*d*₆): signals from a 3-guaiazulenyl group: δ 1.17 (6H, d, J = 7.0 Hz, (CH₃)₂CH-7"), 2.49 (3H, br s, Me-1"), 2.74 (1H, sept, J =7.0 Hz, (CH₃)₂CH-7"), 2.77 (3H, s, Me-4"), 6.56 (1H, d, J =10.4 Hz, H-5"), 6.98 (1H, dd, J = 10.4, 2.0 Hz, H-6"), 7.88 (1H, br s, H-2"), and 7.91 (1H, d, J = 2.0 Hz, H-8"); signals from a 2-thienyl group: δ 6.72 (1H, dd, J = 5.0, 3.4 Hz, H-4'), 6.77 (1H, br d, J = 5.0 Hz, H-5'), and 6.78 (1H, br d, J =3.4 Hz, H-3'); and signals from a (2*E*,4*Z*)-1,3-butadiene unit: δ 6.59 (1H, br d, J = 15.2 Hz, H-1), 6.87 (1H, br dd, J = 15.2, 10.6 Hz, H-2), 6.35 (1H, br dd, J = 10.8, 10.6 Hz, H-3), and 7.22 (1H, br d, J = 10.8 Hz, H-4).



Figure 1. The UV-vis spectra of 1E (a) and 2E (b) in dichloromethane (= CH_2Cl_2). Concentrations, 1E: 0.10 g L⁻¹ (301 µmol), 2E: 0.10 g L⁻¹ (326 µmol). Length of cell, 0.1 cm each. Each log ε value is given in parenthesis.

Table 1. The ¹ H NMR Spectral Data (δ) of 1E , 2E , and
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	3-Guaiazulenyl group								
Compound	Me-1"	H-2″	Me-4"	H-5″	H-6″	(CH ₃) ₂ CH-7"	(CH ₃) ₂ CH-7"	H-8″	
1E	2.49	7.89	2.69	6.54	6.96	2.69	1.16	7.92	
2 E	2.51	7.81	2.79	6.53	6.97	2.71	1.18	7.95	
19	2.52	8.18	3.27	8.34	8.29	3.43	1.43	8.52	
	2-Thienyl group			Butadiene, ethylene, and propenylium units				_	
	H-3'	H-4'	H-5'	H-1	H-2	Н-3	H-4	-	
1E	6.81	6.73	6.75	6.69	6.84	7.07	7.57		
2 E	6.91	6.79	6.81	7.11	8.07	—			
19	7.56	7.19	7.75	7.85	7.63	8.44 ^{b)}	—		

a) Measurement solvent: benzene- d_6 (=C₆D₆) for **1E** and **2E**; acetonitrile- d_3 (=CD₃CN) for **19**. For comparative purposes on the ¹H NMR chemical shifts (δ) of **1E**, **2E**, and **19**, the numbering scheme of **19** was changed as shown in Scheme 7. b) HC⁺- α .

Reaction of (2E,4E)-1-(3-Guaiazulenyl)-4-(2-thienyl)-1,3butadiene (1E) with Tetracyanoethylene (=TCNE). To a solution of compound 1E (10 mg, 30 µmol) in benzene (2 mL) was added a solution of TCNE (9 mg, 60 µmol) in benzene (2 mL) under argon, turning the green solution of 1E into a blue solution, rapidly. The mixture was stirred at 25 °C for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane–ethyl acetate– benzene (2:1:1, vol/vol/vol) as an eluant. The crude product *cis*-4,4,5,5-tetracyano-3-(3-guaiazulenyl)-6-(2-thienyl)-1cyclohexene (11) (11 mg, 23 µmol, 77% yield) was recrystallized from hexane–benzene (5:1, vol/vol) (several times) to provide pure 11 (7 mg, 16 µmol, 55% yield) as crystals.

Compound **11**: Dark-blue blocks $[R_f = 0.33$ on silica gel TLC (solv. hexane:ethyl acetate = 3:1, vol/vol)]; mp 185 °C; exact EI-MS (70 eV): found: m/z 460.1722; calcd for C₂₉H₂₄-N₄S: M⁺, m/z 460.1720; IR v_{max}/cm^{-1} (KBr): 2249 (C=N); 700 MHz ¹H NMR (dichloromethane- d_2): signals from a 3-guaiazulenyl group: δ 1.39 (6H, d, J = 7.0 Hz, (CH₃)₂CH-7"), 2.66 (3H, br s, Me-1"), 3.12 (3H, s, Me-4"), 3.14 (1H, sept, J = 7.0 Hz, (CH₃)₂CH-7"), 7.17 (1H, d, J = 10.8 Hz, H-5"), 7.58 (1H, dd, J = 10.8, 2.2 Hz, H-6"), 7.76 (1H, br s, H-2"), and 8.32 (1H, d, J = 2.2 Hz, H-8"); signals from a 2-thienyl

group: δ 7.19 (1H, dd, J = 5.1, 3.6 Hz, H-4'), 7.40 (1H, br d, J = 3.6 Hz, H-3'), and 7.53 (1H, dd, J = 5.1, 1.1 Hz, H-5'); and signals from a cis-3,6-disubstituted 4,4,5,5-tetracyano-1-cyclohexene unit: δ 4.96 (1H, ddd, J = 2.5, 2.3, 2.3 Hz, H-3), 5.84 (1H, ddd, J = 2.5, 2.3, 2.3 Hz, H-6), 6.15 (1H, ddd, J = 10.4, J)2.5, 2.3 Hz, H-4), and 6.33 (1H, ddd, J = 10.4, 2.5, 2.3 Hz, H-5); 176 MHz ¹³C NMR (dichloromethane- d_2): δ 144.1 (C-4"), 142.4 (C-7"), 139.3 (C-8a"), 137.3 (C-2"), 135.5 (C-6"), 134.7 (C-8"), 134.4 (C-2'), 133.7 (C-3a"), 130.5 (C-5), 129.6 (C-5"), 129.1 (C-3'), 127.6 (C-5'), 127.5 (C-4'), 125.4 (C-1"), 124.8 (C-4), 115.4 (C-3"), 110.9, 110.7, 109.8, 109.5 (CN each), 47.5 (C-1), 47.4 (C-2), 42.8 (C-3), 40.5 (C-6), 37.4 ((CH₃)₂CH-7"), 27.5 (Me-4"), 23.9 ((CH₃)₂CH-7"), and 12.4 (Me-1"). For comparative purposes on the ¹H and ¹³C NMR chemical shifts (δ) of **1E** and **11**, the H and C numbers of the molecular structure 11 were changed as above.

Reaction of (2E,4E)-1-(3-Guaiazulenyl)-4-(2-thienyl)-1,3butadiene (1E) with Dimethyl Acetylenedicarboxylate (=DMAD). To a solution of compound 1E (70 mg, 210 µmol) in toluene (10 mL) was added a solution of DMAD (51 µL, 420 µmol) under argon. The mixture was stirred at reflux temperature (120 °C) for 24 h under argon. After the reaction, the reaction solution was evaporated in vacuo. The residue thus obtained was carefully separated by silica gel col-

Common d	3-Guaiazulenyl group								
Compound	C-1″	Me-1"	C-2″	C-3″	C-3a''	C-4″	Me-4"		
1E	126.7	13.1	136.3	127.2	133.3	146.5	28.4		
2 E	126.4	13.0	136.3	126.4	133.4	146.3	28.3		
19	143.0	13.8	139.6	138.8	151.6	156.8	29.4		
	3-Guaiazulenyl group								
-	C-5″	C-6″	C-7″	(CH ₃) ₂ <i>C</i> H-7"	(<i>C</i> H ₃) ₂ CH-7"	C-8″	C-8a″		
1E	127.7	134.9	141.2	37.9	24.4	133.6	141.8		
2 E	127.8	134.8	140.9	37.9	24.4	133.6	141.4		
19	148.7	144.2	168.5	40.0	23.8	139.6	159.9		
		2-Tł	nienyl group						
	C-2'	C-3′	C-4′	C-5′	-				
1E	144.2	125.4	127.7	123.8					
2 E	145.3	124.6	127.8	122.9					
19	142.5	135.0	130.5	134.3					
	Butad	iene, ethyler	ne, and prope	_					
	C-1	C-2	C-3	C-4					
1E	123.3	127.5	131.3	130.9					
2 E	120.2	126.7	_	—					
19	145.3	126.8	150.8 ^{b)}	—					

Table 2. The ¹³C NMR Spectral Data (δ) of 1E, 2E, and 19^a)

a) Measurement solvent: benzene- d_6 (=C₆D₆) for **1E** and **2E**; acetonitrile- d_3 (=CD₃CN) for **19**. For comparative purposes on the ¹³C NMR chemical shifts (δ) of **1E**, **2E**, and **19**, the numbering scheme of **19** was changed as shown in Scheme 7. b) HC⁺- α .

umn chromatography with hexane–ethyl acetate (4:1, vol/vol) as an eluant (several times), providing pure dimethyl *cis*-3-guaiazulenyl-6-(2-thienyl)-1,4-cyclohexadiene-1,2-dicarboxy-late (**16**) (49 mg, 100 μ mol, 71% yield) as a paste.

Compound 16: Blue paste $[R_f = 0.34$ on silica gel TLC (solv. hexane:ethyl acetate = 4:1, vol/vol)]; exact EI-MS (70 eV): found: m/z 474.1865; calcd for C₂₉H₃₀O₄S: M⁺, m/z 474.1869; 700 MHz ¹H NMR (benzene- d_6): signals from a 3guaiazulenyl group: δ 1.18 (6H, d, J = 7.0 Hz, (CH₃)₂CH-7"), 2.48 (3H, br s, Me-1"), 2.75 (1H, sept, J = 7.0 Hz, (CH₃)₂CH-7"), 2.87 (3H, s, Me-4"), 6.71 (1H, d, J = 10.9 Hz, H-5"), 7.11 (1H, dd, J = 10.9, 1.9 Hz, H-6"), 8.05 (1H, d, J = 1.9 Hz, H-8"), and 8.06 (1H, br s, H-2"); signals based on a 2-thienyl group: δ 6.77 (1H, dd, J = 5.0, 3.2 Hz, C-4'), 6.90 (1H, dd, J = 5.0, 1.1 Hz, H-5', and 7.01 (1H, br d, J = 3.2 Hz, H-3'); signals from a *cis*-3.6-disubstituted 1.2-dimethoxycarbonyl-1,4-cyclohexadiene unit: δ 3.05, 3.36 (3H each, s, H₃COOC-1 or 2), 4.84 (1H, m, H-3), 5.55, 5.57 (1H each, m, H-5 or 6), and 5.74 (1H, m, H-4); 176 MHz ¹³C NMR (benzene- d_6): δ 167.9, 167.8 (H₃COOC-1 or 2), 145.6 (C-2'), 144.4 (C-4"), 139.8 (C-2",7",8a"), 136.9 (C-2), 134.8 (C-1), 134.3 (C-6"), 133.7 (C-8"), 131.8 (C-3a"), 128.4 (C-4), 127.3 (C-5"), 126.8 (C-4'), 126.1 (C-3'), 125.4 (C-1"), 125.1 (C-5'), 123.2 (C-5), 51.5 (H₃COOC-1 and 2) 39.2 (C-3), 38.6 (C-6), 37.8 ((CH₃)₂CH-7"), 27.3 (Me-4"), 24.5 ((CH₃)₂CH-7"), and 13.1 (Me-1"). The C-3" carbon signal was included in other carbon signals. For comparative purposes on the ¹H and ¹³C NMR chemical shifts (δ) of 1E, 11, and 16, the H and C numbers of the molecular structure 16 were changed as above.

Reaction of Dimethyl cis-3-Guaiazulenyl-6-(2-thienyl)-1,4-cyclohexadiene-1,2-dicarboxylate (16) with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (=DDQ). To a solution of compound 16 (78 mg, 160 µmol) in benzene (5 mL) was added a solution of DDQ (54 mg, 160 µmol) in benzene (5 mL) under aerobic conditions. The mixture was stirred at 60 °C for 24 h under aerobic conditions. After the reaction, diethyl ether (5 mL) was added to the mixture and then, the obtained organic layer was washed with NaOH aq (1 M, 3 mL) and distilled water. The extract was dried (MgSO₄), and concentrated in vacuo. The residue thus obtained was carefully separated by silica gel column chromatography with hexane-ethyl acetate (1:1, vol/vol) as an eluant. The crude product cis-3-(3-formyl-5-isopropyl-8-methylazulen-1-yl)-6-(2-thienyl)-1,4-cyclohexadiene-1,2-dicarboxylate (18) was recrystallized from hexanediethyl ether (5:1, vol/vol) (several times) to provide a pure 18 (8 mg, 17 µmol, 11% yield) as crystals.

Compound **18**: Dark-purple blocks [$R_f = 0.47$ on silica gel TLC (solv. hexane:ethyl acetate = 1:1, vol/vol)]; exact EI-MS (70 eV): found: m/z 488.1658; calcd for C₂₉H₂₈O₅S: M⁺, m/z 488.1657; 500 MHz ¹H NMR (CD₂Cl₂): signals based on a 3-substituted 3-formyl-5-isopropyl-8-methylazulen-1-yl: δ 1.39 (6H, d, J = 6.9 Hz, (CH₃)₂CH-7"), 3.15 (3H, s, Me-4"), 3.19 (1H, sept, J = 6.9 Hz, (CH₃)₂CH-7"), 7.45 (1H, d, J = 10.6 Hz, H-5"), 7.66 (1H, dd, J = 10.6, 2.2 Hz, H-6"), 8.16 (1H, br s, H-2"), 9.76 (1H, d, J = 2.2 Hz, H-8"), and 10.19 (1H, s, 1"-CHO); signals from a 2-thienyl group: δ 6.98 (1H, dd, J = 5.0, 4.8 Hz, H-4'), 7.00 (1H, br d, J = 4.8 Hz, H-3'), and 7.30 (1H, dd, J = 5.0, 1.4 Hz, H-5'); and signals from a *cis*-3,6-disubsti-



Figure 2. The UV–vis spectrum of **19** in CH₃CN. Concentration, **19**: 0.10 g L^{-1} (215 µmol). Length of Cell, 0.1 cm. Each log ε value is given in parenthesis.

tuted 1,2-dimethoxycarbonyl-1,4-cyclohexadiene unit: δ 3.43, 3.66 (3H each, s, H₃COOC-1 or 2), 4.85 (1H, m, H-3), 5.49 (1H, m, H-6), 5.81 (1H, m, H-5), and 5.95 (1H, m, H-4). For comparative purposes on the ¹H NMR chemical shifts (δ) of **16** and **18**, the H numbers of the molecular structure **18** were changed as above.

Preparation of (3-Guaiazulenyl)[(*E*)-2-(2-thienyl)ethenyl]methylium Hexafluorophosphate (19). To a solution of guaiazulene (3) (90 mg, 450 μ mol) in methanol (3 mL) was added a solution of (*E*)-2-(2-thienyl)ethylene-1-carbaldehyde (7) (55 mg, 400 μ mol) in methanol (1 mL) containing hexafluorophosphoric acid (i.e., 65% HPF₆ aqueous solution, 0.1 mL). The mixture was stirred at 25 °C for 1 h, precipitating a dark-green solid of **19** and then, the reaction solution containing a precipitate, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile– diethyl ether (1:5, vol/vol) under aerobic conditions (several times) to provide pure **19** as single crystals (175 mg, 377 μ mol, 94% yield).

Compound 19: Dark-green blocks; mp >193 °C (decomp); Found: C, 55.19; H, 4.36%. Calcd for C22H23OF6PS (i.e., $C_{22}H_{23}S + PF_6 + 1/2O_2$): C, 55.00; H, 4.83%;²⁹ exact FAB-MS (3-nitrobenzyl alcohol matrix): found: m/z 391.1515; calcd for C₂₂H₂₃S: $[M - PF_6]^+$, m/z 319.1516; IR ν_{max}/cm^{-1} (KBr): 837 and 559 (PF₆⁻); UV–vis λ_{max}/nm (log ε) in CH₃CN: 242 (4.55), 343 (4.24), and 540 (4.76). Details are shown in Figure 2; 700 MHz ¹H NMR (acetonitrile-d₃): signals from a 3-guaiazulenvlmethvlium ion unit: δ 1.43 (6H, d, J = 6.7 Hz, (CH₃)₂CH-7"), 2.52 (3H, br s, Me-1"), 3.27 (3H, s, Me-4"), 3.43 (1H, sept, J = 6.7 Hz, (CH₃)₂CH-7"), 8.18 (1H, br s, H-2"), 8.29 (1H, dd, J = 11.0, 2.2 Hz, H-6"), 8.34 (1H, d, J =11.0 Hz, H-5"), 8.44 (1H, br d, J = 11.6 Hz, HC⁺- α), and 8.52 (1H, d, J = 2.2 Hz, H-8"); signals from an (E)-1-(2-thienyl)ethenyl group: δ 7.19 (1H, dd, J = 5.0, 3.6 Hz, H-4'), 7.56 (1H, br d, J = 3.6 Hz, H-3'), 7.63 (1H, dd, J = 14.6, 11.6 Hz, H-2), 7.75 (1H, br d, J = 5.0 Hz, H-5'), and 7.85 (1H, d, J = 14.6Hz, H-1); 176 MHz 13 C NMR (acetonitrile- d_3): δ 168.5 (C-7"), 159.9 (C-8a''), 156.8 (C-4''), 151.6 (C-3a''), 150.8 (HC⁺- α), 148.7 (C-5"), 145.3 (C-1), 144.2 (C-6"), 143.0 (C-1"), 142.5 (C-2'), 139.6 (C-2",8"), 138.8 (C-3"), 135.0 (C-3'), 134.3 (C-5'), 130.5 (C-4'), 126.8 (C-2), 40.0 ((CH₃)₂CH-7"), 29.4

(Me-4"), 23.8 ((CH₃)₂CH-7"), and 13.8 (Me-1"). For comparative purposes on the ¹H and ¹³C NMR chemical shifts (δ) of **1E**, **2E**, and **19** (Tables 1 and 2), the numbering scheme of **19** was changed as shown in Scheme 7.

Reduction of (3-Guaiazulenyl)[(*E*)-2-(2-thienyl)ethenyl]methylium Hexafluorophosphate (19) with NaBH₄. To a solution of 19 (31 mg, 90 μ mol) in acetonitrile (2 mL) was added a solution of NaBH₄ (4 mg, 100 μ mol) in ethanol (1 mL). The mixture was stirred at 25 °C for 1 h and then, the reaction solution, of which was 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 (several times), giving pure (*E*)-1-[(3-guaiazulenyl)methyl]-2-(2-thienyl)ethylene (20) as a green paste (20 mg, 56 μ mol, 63% yield).

Compound 20: Green paste; exact EI-MS (70 eV), found: m/z 320.1599; calcd for C₂₂H₂₄S: M⁺, m/z 320.1599; 500 MHz ¹HNMR (benzene- d_6): signals from a 3-guaiazulenylmethyl group: δ 1.21 (6H, d, J = 6.8 Hz, (CH₃)₂CH-7"), 2.57 (3H, br s, Me-1"), 2.75 (3H, s, Me-4"), 2.77 (1H, sept, J =6.8 Hz, $(CH_3)_2CH-7''$), 3.91 (2H, br dd, J = 5.4, 1.8 Hz, 1-CH₂-3"), 6.66 (1H, d, J = 10.3 Hz, H-5"), 7.10 (1H, dd, J =10.3, 2.3 Hz, H-6"), 7.47 (1H, br s, H-2"), and 8.12 (1H, d, J = 2.3 Hz, H-8"); signals from a 2-thienyl group: δ 6.44 (1H, br d, J = 3.4 Hz, H-3'), 6.59 (1H, dd, J = 5.1, 3.4 Hz, H-4'), and 6.67 (1H, br d, J = 5.1 Hz, H-5'); signals based on an (E)ethylene unit: δ 6.27 (1H, dt, J = 15.7, 1.8 Hz, H-2) and 6.44 (1H, dt, J = 15.7, 5.4 Hz, H-1); 125 MHz ¹³C NMR (benzene d_6): δ 145.3 (C-4"), 143.4 (C-2'), 141.2 (C-2"), 138.8 (C-8a"), 138.1 (C-7"), 134.6 (C-6"), 133.7 (C-3a"), 133.4 (C-8"), 127.3 (C-4'), 126.6 (C-3"), 126.5 (C-5"), 124.9 (C-1,3',1"), 124.5 (C-2), 123.3 (C-5'), 37.9 ((CH₃)₂CH-7"), 34.7 (2-CH₂-3"), 26.4 (Me-4"), 24.6 ((CH₃)₂CH-7"), and 13.0 (Me-1").

X-ray Crystal Structure of (2E,4E)-1-(3-Guaiazulenyl)-4-(2-thienyl)-1,3-butadiene (1E). The X-ray measurement of the single crystal 1E was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo K α radiation ($\lambda =$ 0.71075 Å) at -173 °C. The structure was solved by direct methods (SIR92)³⁰ and expanded using Fourier techniques (DIRDIF99).³¹ 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 CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-795121 for compound No. 1E. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for **1E**: $C_{23}H_{24}S$ (FW = 332.50), Dark-green needle (crystal size, $0.66 \times 0.10 \times 0.07 \text{ mm}^3$), triclinic, $P\bar{1}$ (#2), a = 9.7363(7) Å, b = 13.7993(12) Å, c = 14.7729(10) Å, $\alpha = 77.118(7)^\circ$, $\beta = 71.400(6)^\circ$, $\gamma = 82.803(8)^\circ$, V = 1830.6(2) Å³, Z = 4, $D_{calcd} = 1.206 \text{ g cm}^{-3}$, μ (Mo K α) = 1.772 cm⁻¹, measured reflections = 22277, observed reflections = 15514, no. of variables = 482, R1 = 0.0700, wR2 = 0.1508, goodness of fit indicator = 0.978.

Atom	1 E	2E	19	Atom	1E	2E	19
C1″–C2″	1.368(3)	1.373(5)	1.363(8)	C1–C2	1.354(3)	1.337(5)	1.338(8)
C2''-C3''	1.430(4)	1.431(5)	1.441(8)	C2–C3	1.426(3)		$1.421(7)^{a}$
C3''–C3a''	1.419(3)	1.414(5)	1.478(7)	C3–C4	1.349(3)	—	_
C3a''-C4''	1.409(4)	1.408(5)	1.362(8)	C1–C2′	1.433(2)	1.446(5)	1.442(7)
C4''-C5''	1.395(3)	1.384(5)	1.429(8)	C2–C3″		1.450(4)	
C5''-C6''	1.403(3)	1.408(5)	1.376(8)	C4–C3″	1.447(3)		$1.401(8)^{b}$
C6''-C7''	1.378(4)	1.388(5)	1.378(8)	C2'-C3'	1.405(3)	1.371(5)	1.402(8)
C7''–C8''	1.405(4)	1.391(5)	1.392(7)	C3'-C4'	1.409(3)	1.406(5)	1.434(8)
C8''-C8a''	1.369(3)	1.383(5)	1.389(7)	C4'-C5'	1.377(4)	1.350(6)	1.334(9)
C8a''-C1''	1.424(4)	1.424(5)	1.446(7)	S1'-C2'	1.728(3)	1.727(4)	1.733(6)
C8a''–C3a''	1.505(3)	1.498(4)	1.494(7)	S1'–C5'	1.712(2)	1.716(4)	1.719(6)

Table 3. The Selected C–C and C–S Bond Lengths (Å) of 1E, 2E, and 19

a) C2–C α . b) C α –C3". For comparative purposes on the C–C and C–S bond lengths (Å) of **1E**, **2E**, and **19**, the numbering scheme of **19** was changed as shown in Figure 5a.

X-ray Crystal Structure of (3-Guaiazulenyl)[(*E*)-2-(2-thienyl)ethenyl]methylium Hexafluorophosphate (19). The X-ray measurement of the single crystal 19 was made on a Rigaku Saturn CCD area detector with graphite monochromated MoK α radiation ($\lambda = 0.71075$ Å) at -173 °C. The structure was solved by direct methods (SIR92)³⁰ and expanded using Fourier techniques (DIRDIF99).³¹ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix leastsquares refinement was based on F^2 . All calculations were performed using the CrystalStructure crystallographic software package developed by Rigaku corporation, Japan. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-851608 for compound No. 19.

Crystallographic data for **19**: C₂₂H₂₃F₆PS (FW = 464.45), Dark-green plate (crystal size, 0.312 × 0.106 × 0.067 mm³), triclinic, $P\bar{1}$ (#2), a = 8.3551(5) Å, b = 11.4244(9) Å, c = 23.3622(19) Å, $\alpha = 82.906(6)^{\circ}$, $\beta = 82.814(6)^{\circ}$, $\gamma = 77.307(6)^{\circ}$, V = 2147.7(3) Å³, Z = 4, $D_{calcd} = 1.436$ g cm⁻³, μ (Mo K α) = 2.826 cm⁻¹, measured reflections = 24376, observed reflections = 6323, no. of variables = 564, R1 = 0.1393, wR2 = 0.3644, goodness of fit indicator = 0.868. For comparative purposes on the C–C and C–S bond lengths (Å) of **1E**, **2E**, and **19** (Table 3), the numbering scheme of **19** was changed as shown in Figure 5a.

Results and Discussion

Preparation of 1E. Quite recently, we reported the crystal structures and the spectroscopic, chemical, and electrochemical properties as well as a preparation of the 2-thienyl- and 3-guaiazulenyl-substitued (*E*)-ethylene **2E** (Chart 1) (36% yield) and its *Z* geometric isomer **2Z** (24% yield) using the Wittig reaction.¹⁹ For a comparative purpose, a new 2-thienyl- and 3-guaiazulenyl-substituted (2*E*,4*E*)-1,3-butadiene **1E** (Chart 1) was prepared, in 70% yield, using the Wittig reaction shown in Scheme 1. The molecular structure of **1E** was established on the basis of spectroscopic data [exact EI-MS, IR, UV–vis, and ¹H and ¹³C NMR including 2D NMR (i.e., DQF COSY, HSQC, and HMBC)]. Along with the above results, the ¹H NMR signals from the other geometric isomer of **1E**, i.e., (2*E*,4*Z*)-1-(3-guaiazulenyl)-4-(2-thienyl)-1,3-butadiene (**1Z**), were ob-

served by spectral analysis of the product **1** (80% isolated yield) (Scheme 1), while the isomer **1Z** could not be isolated using silica gel column chromatography and recrystallization (several times). Thus, each yield of the (2E,4E)-form **1E** (70%) and the (2E,4Z)-form **1Z** (10%) was calculated from relative intensities for the 700 MHz ¹H NMR signals of an inseparable mixture of the two geometric isomers **1E** and **1Z**.

Reaction of 1E with TCNE. Ouite recently, we reported that the reaction of **2E** with 2 equivalents of TCNE in benzene at 25 °C for 24 h under argon gave a unique product 8 (Chart 2), possessing an interesting molecular structure, in 42% yield as single crystals.¹⁹ while the reaction of 2E with an equivalent of TCNE in DMF at 25 °C for 24 h under argon afforded a structurally unique product 9 (Chart 2) in 19% yield as single crystals which showed dichroism (i.e., the two colors of green and reddish-orange).¹⁹ The molecular structures of the products 8 and 9 were determined by spectroscopic and X-ray crystallographic analyses and further, a reaction mechanism for the formation of **8** and **9** was proposed.¹⁹ For comparative purposes, the reaction of 1E with 2 equivalents of TCNE in benzene was carried out under the same reaction conditions as for 2E. As a result, this reaction did not give a structurally unique product 10, which is a similar molecular structure to 8; however, it afforded a new $[\pi 4 + \pi 2]$ cycloaddition product 11, in 55% isolated yield, as crystals (i.e., dark-blue blocks) (Scheme 2). The molecular structure of 11 was established on the basis of exact EI-MS, IR, and ¹H and ¹³C NMR spectroscopic analyses. Along with the above reaction in benzene, the reaction of 1E with an equivalent of TCNE in DMF was carried out under the same reaction conditions as for 2E. As a result, this reaction did not give a structurally unique product 12, which is a similar molecular structure to 9, while it also afforded a product 11, selectively (Scheme 3). We now propose a reaction mechanism for the formation of 11 according to the following experimental results: namely, to a solution of 1E in benzene (or in DMF) was added a solution of TCNE in benzene (or in DMF) under argon, turning the green solution of 1E into a blue solution of 11, rapidly. Therefore, a reaction pathway for the formation of 11 can be inferred that compound 11 is produced presumably by the Diels–Alder (i.e., the $[\pi 4 + \pi 2]$ cycloaddition) reaction of 1E with TCNE (Schemes 2 and 3) under kinetic control. In relation to our basic study, in 1990 O'Shea and Foote reported



Scheme 1. The preparations of the Wittig reagent $5^{15,16}$ and the aldehyde compound 7^{28} and further, the Wittig reaction of 7 with 5 in ethanol (=C₂H₅OH) in the presence of sodium ethoxide (=NaOC₂H₅) at 25 °C for 24 h under argon, yielding the product 1 in 80% yield.



Scheme 2. The reaction of 1E with 2 equivalents of TCNE in benzene at 25 °C for 24 h under argon gives 11.

that the reaction of (2E,4E)-2,4-hexadiene with TCNE in CH₂Cl₂ at 25 °C yields the Diels–Alder adduct, 1,1,2,2-tetracyano-*cis*-3,6-dimethyl-4-cyclohexene, quantitatively (>99.5% yield).³² The partial structure *cis*-3,6-disubstituted 1,1,2,2-tetracyano-4-cyclohexene, established on the basis of ¹HNMR spectral analysis, coincided with that of **11**.

Reaction of 1E with DMAD. In 2003 Ghosh et al. reported that the reaction of **13** with dimethyl acetylenedicarboxylate

(=DMAD) in toluene at 140 °C for 24 h gives a Diels– Alder-type cycloaddition product 14, in 83% yield, which upon oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (=DDQ) in benzene at 60 °C for 24 h affords a dehydrogenation product 15 in 72% yield (Scheme 4).³³ We have been particularly interested in the above reactions. For comparative purposes, the reaction of 1E with DMAD at 120 °C for 24 h under argon was carried out (Scheme 5), the reaction, of which



Scheme 3. The reaction of 1E with an equivalent of TCNE in DMF at 25 °C for 24 h under argon affords 11.



Scheme 4. The reaction of 13 with DMAD in toluene at 140 °C for 24 h gives 14^{33} which upon oxidation with DDQ in benzene at 60 °C for 24 h affords 15^{33} .



Scheme 5. The reaction of 1E with DMAD in toluene at $120 \,^{\circ}$ C for $24 \,h$ under argon gives 16.

yielded a new Diels–Alder adduct **16**, in 71% isolated yield, as a blue paste. The molecular structure of **16** was established on the basis of exact EI-MS and ¹H and ¹³C NMR spectroscopic analyses. In relation to our basic study, in 1994 Coudert et al. reported that the reactions of the (2E,4E)-1,3-butadiene derivatives with DMAD at 130–150 °C for 15 min–1 h yield similar Diels–Alder adducts to **16** in 51–82% isolated yields.³⁴ Each partial structure *cis*-3,6-disubstituted 1,2-dimethoxycarbonyl-1,4-cyclohexadiene, established on the basis of ¹H NMR spectral analysis, coincided with that of **16**.

Reaction of 16 with DDQ. Similar to Scheme 4, the oxidation of 16 with DDQ in benzene at 60 °C for 24 h under aerobic conditions was carried out, the reaction, of which did not give a similar dehydrogenation product to 15; however, it afforded a new oxygenation product 18, in 11% isolated yield, as crystals (i.e., dark-purple blocks) (Scheme 6). The molecular structure of 18, converting the methyl group substituted at the C-1 position of the 3-guaiazulenyl (=7-isopropyl-1,4-dimeth-ylazulen-3-yl) group into a CHO group, was established on the basis of exact EI-MS and ¹H NMR spectroscopic analyses. Referring the proposed reaction mechanism for the formation

of 3-formyl-5-isopropyl-8-methylazulen-1-yl yielded from the autoxidation of guaiazulene³⁵ (3), a reaction mechanism for the formation of **18** can be inferred as follows: namely, the oxygenation product **18** is derived via (i) the charge-transfer complex **16**⁺⁺•DDQ⁻⁻, (ii) the radical **16**[•] species generated by the deprotonation from the methyl group substituted at the C-1" position of the cation-radical **16**⁺⁺ species, owing to thermo-dynamic control, and finally, (iii) the oxygenation of **16**[•] with oxygen molecule (${}^{3}O_{2}$).²⁰ A preparation of the structurally unique aromatic compound **17**, possessing the 2-thienyl and 3-guaiazulenyl groups at the C-3 and C-6 positions of the 1,2-di(methoxycarbonyl)benzene framework, is further currently under intensive investigation.

Spectroscopic Properties of 1E. The title compound 1E was obtained as dark-green needles. The spectroscopic properties of 1E compared with those of $2E^{19}$ are described as follows: namely, the molecular formula C23H24S was determined by exact EI-MS, whose spectrum showed the M⁺ ion peak based on the molecular structure **1E** illustrated in Chart 1. The IR spectrum of 1E showed specific bands from the C-H, -HC=CH-, C=C, and C-S bonds, the wavenumbers, of which shifted in comparison with those of 2E.¹⁹ The UV-vis spectrum of 1E, compared with that of the starting material guaiazulene³⁶ (3), showed the great difference between the characteristic absorption bands of 3 and those of 1E, suggesting the formation of the molecular structure 1E with an extended π -electron system (Chart 1). The spectral pattern of **1E** resembled that of 2E (Figure 1), while a characteristic absorption band (λ_{max} 437 nm, log $\varepsilon = 4.76$) of **1E** showed a bathochromic shift (Δ 17 nm) and a hyperchromic effect ($\Delta \log \varepsilon = 0.22$) in comparison with the corresponding absorption band (λ_{max} 420 nm, $\log \varepsilon = 4.54$) of **2E**. However, the longest absorption



Scheme 6. The oxidation of 16 with DDQ in benzene at 60 °C for 24 h under aerobic conditions affords 18.



Scheme 7. The reaction of 3 with 7 in methanol (=CH₃OH) containing 65% hexafluorophosphoric acid (=HPF₆) at 25 °C for 1 h gives the corresponding monocarbenium ion compound 19, which upon reduction with sodium borohydride (=NaBH₄) in a mixed solvent of ethanol (=C₂H₅OH) and acetonitrile (=CH₃CN) at 25 °C for 1 h affords the H⁻ reduction product 20. For comparative purposes on the ¹H and ¹³C NMR chemical shifts (δ) of 1E, 2E, and 19, the numbering scheme of 19 was changed as shown in Scheme 7.

band (λ_{max} 645 nm, log $\varepsilon = 2.84$) of **1E** coincided with that $(\lambda_{\text{max}} 644 \text{ nm}, \log \varepsilon = 2.77)$ of **2E**. The ¹H NMR spectrum of 1E showed signals from a 3-guaiazulenyl and 2-thienyl group and signals from a (2E, 4E)-1,3-butadiene unit possessing two nonequivalent substituents at the C-1 and C-4 positions, all the signals, of which were carefully assigned using DQF COSY and computer-assisted simulation based on first-order analysis. As a result, the proton signals (H-1, H-4, H-3', and Me-4") of 1E (Chart 1) showed upfield shifts in comparison with the corresponding signals of 2E, while the proton signals (H-4', H-5', and H-2") of 1E revealed slight chemical shifts in comparison with those of 2E, presumably owing to the difference between an influence of a ring current generated from 1E with a (2E, 4E)-1,3-butadiene linkage and that generated from 2E with an (E)-ethylene linkage. Other signals of 1E coincided with those of 2E (Table 1). The ¹³C NMR spectrum exhibited 21 carbon signals assigned using HSQC and HMBC. As a result, a carbon signal (C-2') and the five carbon signals (C-1, C-4, C-3', C-5', and C-3") of 1E showed chemical shifts in comparison with the corresponding signals of 2E, owing to the same reason described as the above ¹HNMR chemical shifts. Other signals of 1E coincided with those of 2E (Table 2). Thus, the total spectroscopic analyses for 1E led to the molecular structure illustrated in Chart 1, the molecular conformation, of which was supported by NOE measurement.

Preparation and Spectroscopic and Chemical Properties of the Monocarbenium Ion Compound 19. We have been interested further in the great difference between the spectroscopic and electrochemical properties and the crystal structure of a new conjugated (and delocalized) π -electron system 19, possessing a propenium ion linkage, and those of the title conjugated π -electron system 1E, possessing a (2*E*,4*E*)-1,3-butadiene linkage. The target monocarbenium ion compound 19 was prepared according to the procedure shown in Scheme 7. The structure of the product 19 was established on the basis of elemental analysis and spectroscopic data [exact FAB-MS, IR, UV–vis, and ¹H and ¹³C NMR including 2D NMR (i.e., DQF COSY, HSQC, and HMBC)].

Compound **19** (94% isolated yield) was obtained as darkgreen blocks, while a solution of **19** in CH₃CN was purple. An elemental analysis confirmed the formula $C_{22}H_{23}OF_6PS$ (i.e., $C_{22}H_{23}S + PF_6 + 1/2O_2$).²⁹ The formula $C_{22}H_{23}S$ for the monocarbenium ion unit ($[M - PF_6]^+$) was determined by exact FAB-MS spectrum. The IR spectrum showed two specific bands (v_{max} 837 and 559 cm⁻¹) from the counter anion (PF₆⁻). A characteristic UV–vis absorption band from the formation of the (3-Guaiazulenyl)[(*E*)-2-(2-thienyl)ethenyl]methylium ion moiety, with a delocalized π -electron system, appeared at an absorption maximum (λ_{max} 540 nm, log ε = 4.76) (Figure 2), whose specific broad band revealed a larger bathochromic shift $(\Delta \lambda_{\rm max} 103 \,\rm nm)$ in comparison with the corresponding absorption band (λ_{max} 437 nm, log $\varepsilon = 4.76$) of **1E** (Figure 1a); however, its molar extinction coefficient (log ε) of **19** coincided with that of **1E**. The ¹H NMR spectrum showed signals from an (3-Guaiazulenyl)[(E)-2-(2-thienyl)ethenyl]methylium ion moiety, all the signals, of which were carefully assigned using DQF COSY and computer-assisted simulation based on firstorder analysis (Table 1). The ¹³C NMR spectrum exhibited 20 carbon signals assigned by HSOC and HMBC (Table 2). Thus, the elemental analysis and the total spectroscopic analyses for 19 led to the target structure (3-Guaiazulenyl)[(E)-2-(2thienyl)ethenyl]methylium hexafluorophosphate illustrated in Scheme 7, the structural conformation, of which was supported by NOE measurement. Furthermore, all the ¹H NMR signals for the 3-guaiazulenvl and 2-thienvl groups of 19 showed downfield shifts in comparison with those of 1E (Table 1): namely, the order of a larger downfield shift was H-5" ($\Delta \delta$ 1.80 > H-6" (1.33) > H-5' (1.00) > H-3' (0.75) > (CH₃)₂CH-7''(0.74) > H-8''(0.60) > Me-4''(0.58) > H-4'(0.46) > H-2'' $(0.29) > (CH_3)_2$ CH-7" (0.27) > Me-1" (0.03). Moreover, the ¹³C NMR signals for the azulene ring and the thiophene ring (except the C-2' carbon) of 19 revealed downfield shifts in comparison with those of 1E (Table 2): namely, the order of a larger downfield shift was C-7" ($\Delta \delta$ 27.3) > C-5" (21.0) > C-3a'' (18.3) > C-8a'' (18.1) > C-1'' (16.3) > C-3'' (11.6) > C-5' (10.5) > C-4'' (10.3) > C-3' (9.6) > C-6'' (9.3) > C-8''(6.0) > C-2'' (3.3) > C-4' (2.8) > C-2' (-1.7). Thus, the detailed NMR spectral analyses of 19, compared with those of 1E. suggested the formation of the monocarbenium ion compound 19 with the two representative resonance structures of 19a and 19b (Chart 3). Along with the above results and discussion, the reduction of 19 with NaBH₄ in a mixed solvent of ethanol and acetonitrile at 25 °C for 1 h gave the corresponding H⁻ reduction product 20 (Scheme 7), in 63% isolated yield, as a green paste. The molecular formula C₂₂H₂₄S was determined by exact EI-MS spectrum. The ¹H NMR spectrum showed signals from a 2-thienyl and (3-guaiazulenyl)methyl group and an (E)-ethylene unit, all the signals, of which were carefully assigned using similar analyses to those of 19. The ¹³C NMR spectrum exhibited 19 carbon signals assigned using similar analyses to those of 19. Thus, the total spectroscopic analyses for 20 led to the molecular structure (E)-1-[(3guaiazulenyl)methyl]-2-(2-thienyl)ethylene, in which a hydride ion (=H⁻) attached to the C⁺- α position of 19, selectively. The molecular conformation of 20, illustrated in Scheme 7, was also supported by NOE measurement. Furthermore, from comparative studies on the ¹H and ¹³C NMR chemical shifts (δ) of 19 with those of 20, it can be inferred that a positive charge of the (3-guaiazulenyl)methylium ion unit of 19 is transferred to a guaiazulene (or thiophene) ring, generating a representative resonance structure of 19a (or 19b) (Chart 3). Moreover, from comparative studies of the ¹³CNMR chemical shifts of 1E with those of 20, it was found that the five carbon signals (i.e., C-1", C-4", C-5", C-7", and C-8a") from the guaiazulene ring of 1E showed downfield shifts in comparison with those of 20: namely, the order of a larger downfield shift was C-7" ($\Delta \delta$ 3.1) > C-8a'' (3.0) > C-1'' (1.8) > C-4'' (1.2) and C-5'' (1.2), while a C-2" carbon signal from the guaiazulene ring of 1E revealed a larger upfield shift ($\Delta \delta$ -4.9) in comparison with

that of **20**, presumably owing to the formation of a resonance structure, i.e., the 3-guaiazulenylium ion form, for **1E**. The chemical shifts of other carbon signals for the guaiazulene and thiophene rings of **1E** coincided with those of **20**.

X-ray Crystal Structure of 1E. The recrystallization of 1E from a mixed solvent of chloroform and ethanol (1:5, vol/vol) provided single crystals suitable for X-ray crystallographic analysis. The crystal structure of 1E was then determined by means of X-ray diffraction, producing accurate structural parameters. Similar to $2E^{19}$ (Figure 4b), two molecules of 1E were found to exist in a unit cell of the single crystal (Figure 3b). An ORTEP drawing of 1E with a numbering scheme and the two different ORTEP drawings of 1E are shown in Figures 3a and 3b along with the C-C and C-S bond lengths compared with those of 2E (Table 3). The crystal structures of 1E and 2E supported the molecular conformations illustrated in Chart 1. Previously, it was found that the two aromatic rings of the 2'-thienyl and 3"-guaiazulenyl groups of **2E** twist by 5 and 20° from the plane of the (*E*)–HC=CH– unit (Figure 4a),¹⁹ presumably due to an influence of intermolecular π -stacking. Similar to **2E**, each plane of the 2'-thienyl and 3"guaiazulenyl groups of 1E twisted by 6 and 24° from each plane of the C1-C2 and C3-C4 units, owing to a similar reason to the case of 2E. The structural parameters of 1E showed that the average C-C bond lengths of the seven- and five-membered rings for the 3-guaiazulenvl group of **1E** (1.409 and 1.429 Å) coincide with those of 2E (1.409 and 1.428 Å), while the C1-C2 and C3–C4 bond lengths of 1E (1.354 and 1.349 Å) are longer than the C1–C2 bond length of **2E** (1.337 Å). The bond alternation pattern observed for the 2'-thienyl and 3"-guaiazulenvl groups of 1E coincided with that of 2E. Moreover, the intramolecular S-HC2 distances for the two different ORTEP drawings of 1E (2.78 and 2.72 Å) (Figure 3b) and 2E (2.77 and 2.71 Å) (Figure 4b) were shorter than the sum of the van der Waals radii of the hydrogen and sulfur atoms (1.2 and 1.85 Å), the distances, which were suggested to form an intramolecular S-HC2 hydrogen bond between them. Besides, an intermolecular S.S. distance of 1E (3.90 Å) (Figure 3b) was shorter than that of 2E (4.57 Å) (Figure 4b), both of which were suggested to form a S-S configuration interaction. Along with the ORTEP drawings of 1E and 2E, the crystal packing diagrams of 1E and 2E (Figures 3c and 4c) revealed that each average interplane distance between the overlapping molecules, whose directions are the same, is 3.60 (for 1E) or 3.69 Å (for 2E), suggesting that each molecule forms a π -stacking structure in the single crystal.³⁷

X-ray Crystal Structure of 19. The recrystallization of **19** from a mixed solvent of acetonitrile and diethyl ether (1:5, vol/vol) provided stable single crystals suitable for X-ray crystallographic analysis. The crystal structure of **19** was then determined by means of X-ray diffraction, producing accurate structural parameters. An ORTEP drawing of **19** is shown in Figure 5a along with the C–C and C–S bond lengths compared with those of **1E** (Table 3). As a result, it was found that the planes of the 2'-thienyl group and the (3''-guaiazulenyl)-methylium ion unit of **19** slightly twist by 5 and 2° from the plane of the (*E*)-ethylene unit, in comparison with **1E** and **2E**, due to formation of a delocalized π -electron system. The structural parameters of **19** and **1E** showed that the average C–C



Figure 3. (a, b) The ORTEP drawing (30% probability thermal ellipsoids) of 1E. (c) The crystal packing diagram of 1E.³⁷ Hydrogen atoms are omitted for reasons of clarity.



Figure 4. (a, b) The ORTEP drawing (30% probability thermal ellipsoids) of 2E. (c) The crystal packing diagram of 2E.³⁷ Hydrogen atoms are omitted for reasons of clarity.



Figure 5. (a) The ORTEP drawing of **19** (30% probability thermal ellipsoids). For comparative purposes on the C–C and C–S bond lengths (Å) of **1E**, **2E**, and **19**, the numbering scheme of **19** was changed as shown in Figure 5a. Top (b) and side (c) views for the crystal packing diagram of **19**.³⁷ Hydrogen atoms are omitted for reasons of clarity.

bond lengths for the seven- and five-membered rings of the 3-guaiazulenyl group of 19 (1.403 and 1.445 Å) do not coincide with those of **1E** (1.409 and 1.429 Å), presumably because formation of the three representative resonance structures 19, 19a, and 19b (Chart 3) in a single crystal. The bond alternation pattern observed for the 2'-thienyl and 3"-guaiazulenyl groups of 19 resembled that of 1E, suggesting a contribution of the resonance structures of the 3-guaiazulenylium and 2thienylium ion forms for 1E. Similar to 1E and 2E (Figures 3a and 4a), the S-HC2 distance for the ORTEP drawing of 19 (2.76 Å) (Figure 5a) was shorter than the sum of the van der Waals radii of the hydrogen and sulfur atoms (1.2 and 1.85 Å), the distance, of which was suggested to form an intramolecular S.-HC2 hydrogen bond between them. Along with the ORTEP drawing of 19, the crystal packing diagrams of 19 (Figures 5b and 5c) revealed that each average interplane distance between the overlapping molecules, whose directions are the same, is 8.33 Å (for the intermolecular S-S distance) or 6.92 Å (for the intermolecular C5'...C5' distance).³⁷ From the results, it can be inferred that the interplane distances between the overlapping molecules of 19 are longer than those of 1E and 2E (Figures 3b, 3c, 4b, and 4c), because of electrostatic repulsion between those of 19.

Electrochemical Behavior of 1E. We have been interested further in a comparative study of the electrochemical properties of **1E** with that of **2E**. The electrochemical behavior of **2E** was measured by means of CV (=cyclic voltammogram) and DPV (=differential pulse voltammogram) [potential (in volt) vs. SCE] in CH₃CN containing 0.1 M [*n*-Bu₄N]BF₄ (Figures 6c and 6d). The two redox potentials observed by DPV were positioned at the E_p values of +0.50 and -1.61 V (Figure 6d), while the corresponding one irreversible oxidation potential and one reversible reduction potential determined by CV

were located at +0.50 (E_{pa}), +0.38 (E_{pc}), and -1.65 V ($E_{1/2}$) (Figure 6c). For comparative purposes, the electrochemical properties of 1E were measured under the same conditions as for 2E. Similarly, as in the case of 2E, two redox potentials observed by DPV were positioned at the $E_{\rm p}$ values of +0.42 and -1.63 V (Figure 6b), while the corresponding one irreversible oxidation potential and one reversible reduction potential determined by CV were located at +0.41 (E_{pa}), +0.32 (E_{pc}), and -1.65 V ($E_{1/2}$) (Figure 6a), the results, showed that the reduction potential/V of 1E coincides with that of 2E, however the oxidation potential/V of 1E is slightly lower than that of **2E**. Referring to our previous three papers, 10,15,20 a redox mechanism of 1E based on its CV datum is proposed as illustrated in Scheme 8: namely, 1E is one-electron-oxidized, generating a cation-radical **a** with a representative resonance structure **b**. Furthermore, 1E is one-electron-reduced to the anion-radical c. From the data shown in Figure 6, a similar redox mechanism to 1E can be inferred for 2E. In conclusion, 1E serves as a slightly stronger one-electron donor than 2E and a similar oneelectron acceptor to 2E.

Electrochemical Behavior of 19. Along with the electrochemical behavior of 1E and 2E, we have been interested in the electrochemical properties of 19 for comparative study. The electrochemical behavior of 19 was then measured by CV and DPV [potential (in volt) vs. SCE] in CH₃CN containing 0.1 M [*n*-Bu₄N]BF₄ (Figure 6). One reduction potential observed by DPV was positioned at -0.14 V (Figure 7b) and the corresponding one irreversible reduction potential determined by CV was located at -0.20 V (E_{pc}) (Figure 7a), the results, of which showed that the reduction potential of the extended π -electron system 19 coincides with that of the previously reported (3-guaiazulenyl)(2-thienyl)methylium hexafluorophosphate [i.e., -0.16 V (E_p) by DPV and -0.22 V (E_{pc}) by



Figure 6. Cyclic and differential pulse voltammograms (=CV and DPV) of **1E** (3.0 mg, 8.9 µmol) [see (a), (b)] and **2E** (3.0 mg, 9.8 µmol) [see (c), (d)] in acetonitrile (=CH₃CN) (10 mL) containing 0.1 M tetrabutylammonium tetrafluoroborate (=[n-Bu₄N]BF₄) at glassy carbon (inside diameter: 3 mm) and a platinum wire served as 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 V (E_p) by DPV and +0.42 V ($E_{1/2}$) by CV under the same electrochemical measurement conditions as for **1E** and **2E**.



Scheme 8. A proposed redox mechanism based on the CV datum (Figure 6a) of 1E.



Figure 7. CV and DPV of **19** (3.0 mg, 6.4 μ mol) [see (a), (b)] in CH₃CN (10 mL) containing 0.1 M [*n*-Bu₄N]BF₄ at glassy carbon (inside diameter: 3 mm) and a platinum wire served as working and auxiliary electrodes; scan rates 100 mV s⁻¹ at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (*E*_p) by DPV and +0.40 V (*E*_{1/2}) by CV under the same electrochemical measurement conditions as for **19**.

CV].² From the above results, it can be inferred that the reduction potential $[-0.25 \text{ V} (E_{pc})]$, observed by the CV of **1E** (Figure 6a), arises from the reduction potential/V of the **1E**⁺⁺ species generated by the electrochemical oxidation of **1E**.

Conclusion

We have reported the following four interesting points for the title basic studies: namely, (i) the Wittig reaction of the aldehyde compound 7 with the reagent 5 in ethanol containing NaOC₂H₅ at 25 °C for 24 h under argon gave the two (2*E*,4*E*)and (2*E*,4*Z*)-geometric isomers of a new compound 1-(3guaiazulenyl)-4-(2-thienyl)-1,3-butadiene (1) in 80% yield, the only title (2*E*,4*E*)-form **1E**, of which could be isolated as single crystals; (ii) the reaction of **1E** with TCNE in benzene (or in DMF) at 25 °C for 24 h under argon afforded a new Diels– Alder adduct **11**, in 77% yield, respectively; (iii) the reaction of **1E** with DMAD in toluene at 120 °C for 24 h under argon yielded a new Diels–Alder adduct **16**, in 71% yield, which upon oxidation with DDQ in benzene at 60 °C for 24 h under aerobic conditions provided a new product **18**, converting the methyl group substituted at the C-1 position of the 3-guaiazulenyl group into a CHO group, selectively; and (iv) the spectroscopic properties, the crystal structure, and the electrochemical behavior of the title (2E,4E)-1,3-butadiene derivative **1E** compared with those of the structurally related (E)-ethylene derivative **2E** and new propenium ion derivative **19** were documented.

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29 It has been long-known that guaiazulene (3) gradually undergoes oxygenation even on exposure to air at room temperature.^{21,35} On the other hand, we quite recently found that the mono-¹⁸ and dicarbenium²⁰ ion compounds, stabilized by the 3guaiazulenyl group(s), are recrystallized from acetonitrile–diethyl ether (1:5, vol/vol) under aerobic conditions (several times) to provide single crystals, respectively, containing molecular oxygen. Similar to our previous two papers,^{18,20} the monocarbenium ion compound **19**, stabilized by a 3-guaiazulenyl group, was recrystallized under the same recrystallization conditions as above to provide single crystals containing molecular oxygen.

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37 Although the single crystal of **9** (Chart 2) showed dichroism (i.e., the two colors of green and reddish-orange), the specific phenomenon, of which could be identified using a polarization microscope,¹⁹ the single crystals of **1E**, **2E**, and **19** did not show dichroism.