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Reactions of (*E*)-1,2-di(3-guaiazulenyl)ethylene and 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene with tetracyanoethylene (TCNE) in benzene: comparative studies on the products and their spectroscopic properties

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Abstract—Reactions of the title ethylene derivatives, (*E*)-1,2-di(3-guaiazulenyl)ethylene (**1**) and 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene (**2**), with a 2 M amount of TCNE in benzene at 25 °C for 24 h under argon give new cycloaddition compounds, 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (**3**) from **1** and 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]-azulene (**4**) from **2**, respectively, in 66 and 87% isolated yields. Comparative studies on the above reactions as well as the spectroscopic properties of the unique products **3** and **4**, possessing interesting molecular structures, are reported and, further, a plausible reaction pathway for the formation of these products is described.

1. Introduction

In the previous papers,[1–10] we reported a facile preparation and the crystal structures as well as the spectroscopic, chemical and electrochemical properties of the mono- and dicarbocations stabilized by a 3-guaiazulenyl group. During the course of our investigations, we have recently found (i) that the reduction of the dicarbocation compound, α,α′-bis(3-guaiazulenylmethylium) bis(tetrafluoroborate), with zinc powder in trifluoroacetic acid at 0 °C for 5 min under argon gave (*E*)-1,2-di(3-guaiazulenyl)ethylene (**1**) in 94% isolated yield and, further, the reaction of naturally occurring guaiazulene with 1,2-bis(4-methoxyphenyl)-1,2-ethanediol in methanol in the presence of hydrochloric acid at 60 °C for 3 h under aerobic conditions afforded the pinacol rearrangement product, 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene (**2**), in 97% isolated yield;[8] and (ii) that the oxidation potentials of the above ethylene derivatives **1** and **2** in CH_3CN containing 0.1 M $[n\text{-}Bu_4N]BF_4$ as a supporting electrolyte showed that **1** stepwise underwent two-electron oxidation at +0.20 ($E_{1/2}$, reversible) and +0.35 ($E_{1/2}$, reversible) V by CV (and +0.24 and +0.39 V by DPV), generating an electrochemically stable dication-species and, similarly, **2** stepwise underwent two-electron oxidation at +0.52 ($E_{1/2}$, reversible) and +0.73 ($E_{1/2}$, reversible) V by CV (and +0.55 and +0.76 V by DPV), also generating an electrochemically stable dication-species.[8] Thus, the CV and DPV data suggested **1** and **2** serve as an electron donor, respectively, and indicated **1** is more susceptible two-electron oxidation than **2**. Furthermore, we have quite recently reported that the reactions of the *meso* forms, (1*R*,2*S*)-1,2-di(2-furyl)-1,2-di(3-guaiazulenyl)ethane[10] (**A**) [oxidation potential: +0.48 (E_{pa}, irreversible) V by CV and +0.48 (E_p) V by DPV][11] and (1*R*,2*S*)-1,2-di(3-guaiazulenyl)-1,2-di(2-thienyl)ethane[10] (**B**) [oxidation potential: +0.57 (E_{pa}, irreversible) V by CV and +0.56 (E_p) V by DPV],[11] with a 2 M amount of TCNE, which serves as an electron acceptor [−0.75 ($E_{1/2}$, quasi-reversible) V by CV and −0.76 (E_p) V by DPV][12] in benzene at 25 °C for 5 h (for **A**) and 48 h (for **B**) under

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Keywords: Annulation; Charge-transfer complex; (*E*)-1,2-Di(3-guaiazulenyl)ethylene; 2-(3-Guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene; TCNE.

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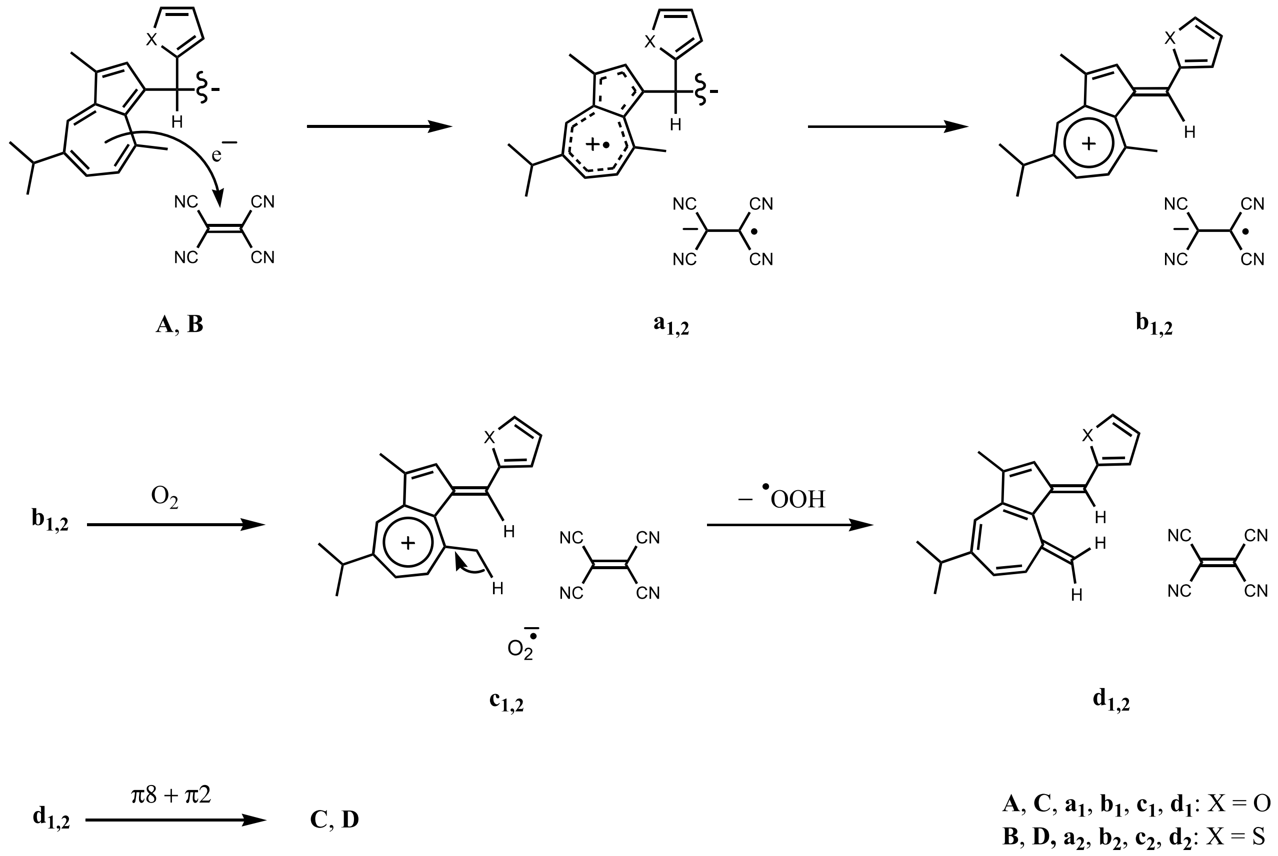


Scheme 1. A plausible reaction pathway for the formation of **C** and **D** yielded by the reactions of the *meso* forms **A** and **B** with a 2 M amount of TCNE in benzene at 25 °C for 5 h (for **A**) and 48 h (for **B**) under oxygen. The partial structures **A**, **B** and $\mathbf{a}_{1,2}$ are illustrated.

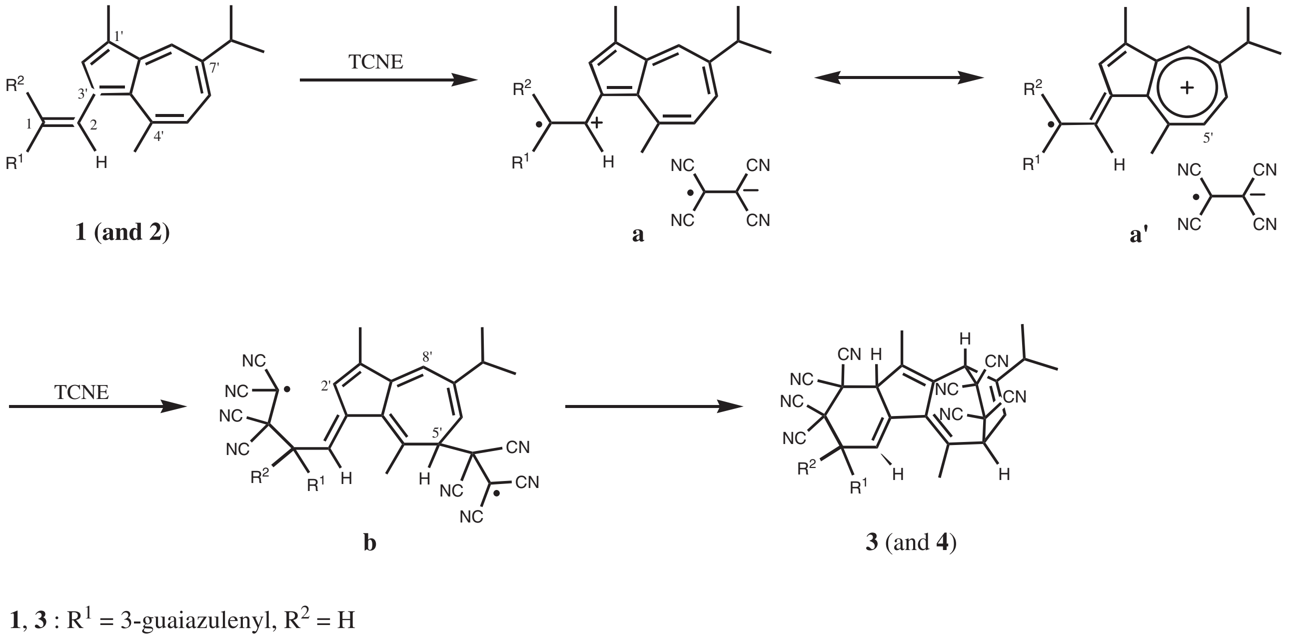
oxygen gave 2,2,3,3-tetracyano-4-(2-furyl)-8-isopropyl-6-methyl-1,2,3,4-tetrahydrocyclohepta[*c*,*d*]azulene (**C**) and 2,2,3,3-tetracyano-8-isopropyl-6-methyl-4-(2-thienyl)-1,2,3,4-tetrahydrocyclohepta[*c*,*d*]azulene (**D**), respectively, in 74 and 21% isolated yields and, further, a plausible reaction pathway for the formation of the unique products **C** and **D**, possessing interesting molecular structures, was described as shown in Scheme 1.[11] Moreover, our interest has quite recently been focused on a comparative study on the title chemistry, the reactions of **1** and **2** with TCNE in benzene at 25 °C under argon. In relation to our basic studies, in 1961 Hafner and Moritz reported that the reaction of guaiazulene in petroleum ether with TCNE in AcOEt at −20 °C gave a 1:1 π-complex in 98% isolated yield, which was converted into 3-tricyanovinylguaiazulene (68% isolated yield) in DMF at room temperature.[13] Furthermore, the addition and cycloaddition reactions of TCNE in organic chemistry[14–18] including azulenes[13,19–21] have been studied to a considerable extent, and a large number of those results and discussion have been well documented. Along with those investigations, we now wish to report the detailed title chemistry, affording the unique products, 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (**3**) from **1** and 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (**4**) from **2**, possessing interesting molecular structures, presumably via charge-transfer and, further, cycloaddtion reactions as shown in Scheme 2.

2. Results and discussion

2.1. Reaction of (*E*)-1,2-di(3-guaiazulenyl)ethylene (1) with TCNE; preparation and spectroscopic properties of 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (3)

Compound **3** was prepared from compound **1** and TCNE using benzene as a solvent as shown in Section 4.1.1, whose molecular structure was established on the basis of elemental analysis and spectroscopic data [UV–vis, IR, exact FAB-MS, ^{1}H and ^{13}C NMR including 2D NMR (i.e., H–H COSY, HMQC = ^{1}H detected hetero nuclear multiple quantum coherence and HMBC = ^{1}H detected hetero nuclear multiple bond connectivity)].

Compound **3** (66% isolated yield) was blue prisms [R_f = 0.39 on silica-gel TLC (hexane/AcOEt = 7:3, vol/vol)], mp 159 °C [decomp., determined by the thermal analysis (TGA and DTA)]. The characteristic UV–vis (CH_2Cl_2) absorption bands based on the 3-guaiazulenyl group were observed and the longest visible absorption wavelength appeared at λ_{max} 587 nm (log ε = 2.62). The IR (KBr) spectrum showed



Scheme 2. A plausible reaction pathway for the formation of **3** and **4** yielded by the reactions of **1** and **2** with a 2 M amount of TCNE in benzene at 25 °C for 24 h under argon.

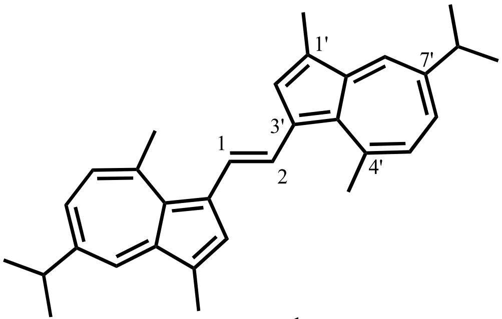
a specific band based on the –C≡N group at ν_{max} 2253 and 2249 cm^{-1}, which coincided with those of **C**[11] and **D**.[11] The protonated molecular formula $C_{44}H_{37}N_8$ ($[M+H]^+$) was determined by the exact FAB-MS (3-nitrobenzyl alcohol matrix) spectrum. The elemental analysis confirmed the molecular formula $C_{44}H_{36}N_8$. The 500 MHz ^1H NMR (CD_2Cl_2) spectrum showed signals based on the structure of 8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydrobenz[*a*]azulene possessing a 3-guaiazulenyl group at the C-3 position, which signals (δ and J values) were carefully assigned using the H–H COSY technique and the computer-assisted simulation analysis (see Section 4.1.1). The 125 MHz ^{13}C NMR (CD_2Cl_2) spectrum exhibited 36 carbon signals (δ) based on the structure of 3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene and eight carbon signals (δ) based on the –C≡N group, bound at the C-1, 2, 11 and 12 positions, assigned by the HMQC and HMBC techniques (see Section 4.1.1). Thus, the elemental analysis and these spectroscopic data for **3** led to a new molecular structure, 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (see Chart 1).

The crystal structure of **3** was then measured by means of the X-ray diffraction. As a result, although an X-ray crystallographic analysis of **3**, producing accurate structural parameters, has not yet been achieved because of very difficulty in obtaining a single crystal suitable for this purpose (see Ref. 22), the molecular structure of **3** established on the basis of elemental analysis and spectroscopic data could be determined. The crystal structure of **3** with the numbering Scheme, indicating the molecular structure, 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene, is shown in Figure 1. An X-ray crystallographic analysis of **3**, producing accurate structural parameters, is further currently under intensive investigation.

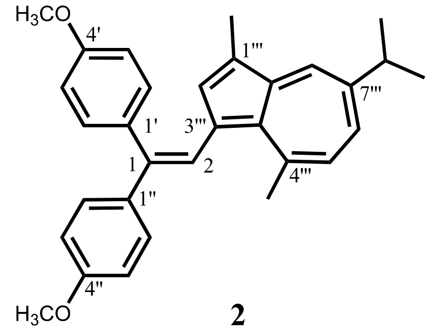
2.2. Reaction of 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene (2) with TCNE; preparation and spectroscopic properties of 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (4)

Similarly, as in the case of the preparation of **3**, the target compound **4** was prepared from compound **2** and TCNE using benzene as a solvent as shown in Section 4.1.2, whose molecular structure was established on the basis of similar elemental and spectroscopic analyses to those of **3**.

Compound **4** (87% isolated yield) was white powder [R_f= 0.18 on silica-gel TLC (hexane/AcOEt=7:3, vol/vol)], mp 140 °C [decomp., determined by the thermal analysis (TGA and DTA)], while a solution of **4** in dichloromethane was pale yellow. The characteristic UV–vis (CH_2Cl_2) absorption bands based on the azulenyl group were not observed and the longest visible absorption wavelength appeared at λ_{max} 410 nm (log ε=3.08). The IR (KBr) spectrum showed a specific band based on the –C≡N group at ν_{max} 2253 and 2249 cm^{-1}, which coincided with that of **3**. The protonated molecular formula $C_{43}H_{33}N_8O_2$ ($[M+H]^+$) was determined by the exact FAB-MS (3-nitrobenzyl alcohol matrix) spectrum. The elemental analysis confirmed the molecular formula $C_{43}H_{34}N_8O_3$ based on the monohydrate of **4**. The 500 MHz ^1H NMR (CD_2Cl_2) spectrum showed signals based on the structure of 8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydrobenz[*a*]azulene possessing two 4-methoxyphenyl groups at the C-3 position, which signals (δ and J values) were carefully assigned using the H–H



1



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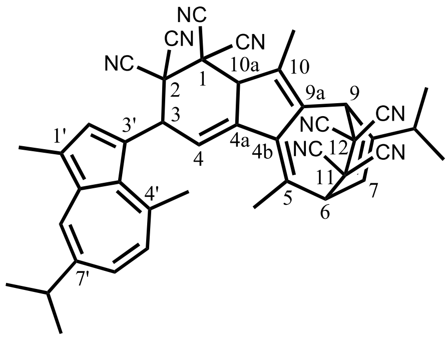

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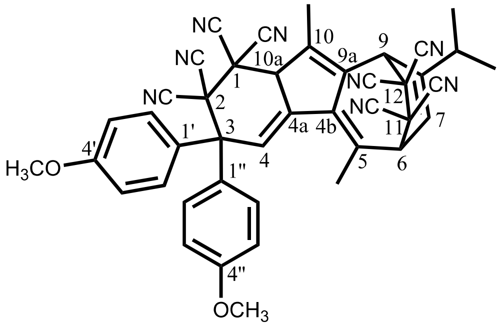
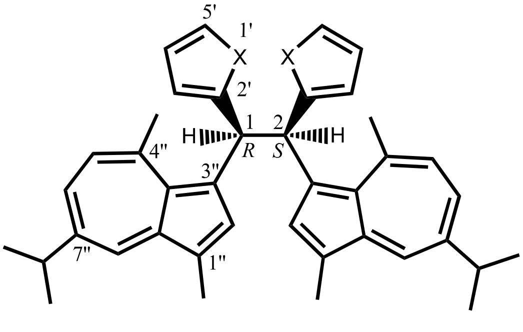
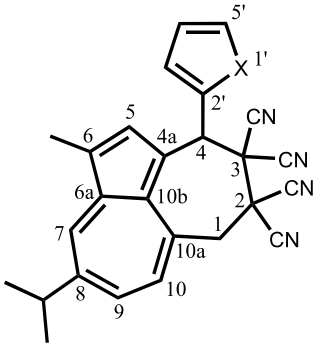


4



A, B



C, D

A, C : X = O
B, D : X = S

Chart 1.

COSY technique and the computer-assisted simulation analysis (see Section 4.1.2). The 125 MHz ^{13}C NMR (CD_2Cl_2) spectrum exhibited 35 carbon signals (δ) based on the structure of 8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene and eight carbon signals (δ) based on the –C≡N group, bound at the C-1, 2, 11 and 12 positions, assigned by the HMQC and HMBC techniques (see Section 4.1.2). Thus, the elemental analysis and these spectroscopic data for **4** led to a new molecular structure, 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (see Chart 1). From a comparative study on the detailed ^{1}H and ^{13}C NMR signals of **3** and **4** (see Sections 4.1.1 and 4.1.2), it can be inferred that the conformation of the 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene unit of **4** assumes similar to that of **3**.

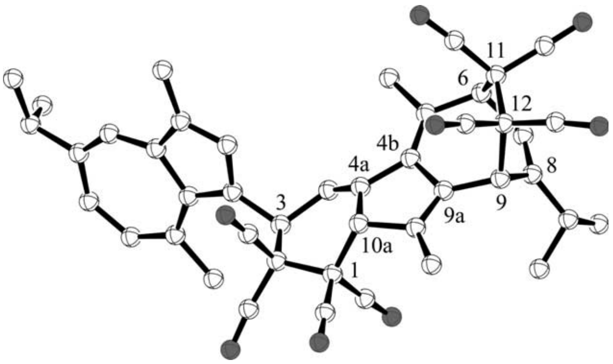


Figure 1. The X-ray crystal structure of **3**. Hydrogen atoms are omitted for reasons of clarity.

2.3. A plausible reaction pathway for the formation of products 3 and 4

From the molecular structures of the resulting products **3** and **4**, obtained by the reactions of the ethylene derivatives **1** and **2**, which serve as an electron donor,[8] with a 2 M amount of TCNE, which serves as an electron acceptor (see Section 1)[12] in benzene at 25 °C for 24 h under argon, a plausible reaction pathway for the formation of compounds **3** and **4** can be inferred as illustrated in Scheme 2; namely, (i) to a solution of TCNE in benzene was added a solution of **1** (and **2**) in benzene under argon, turning the dark-green solution of **1** (and **2**) into a purple solution (for **1**) and into a black solution (for **2**), rapidly. This result suggests that the reaction of **1** (and **2**) with TCNE gives the corresponding charge-transfer (CT) complex **a**, respectively, whose complex has not yet been isolated;[23] and (ii) the above reaction mixture was stirred at 25 °C for 24 h under argon, gradually precipitating a blue solid of **3** from **1**, and gradually precipitating a white solid of **4** from **2**. This result suggests that the CT complex **a** generated is converted into **3** (and **4**) presumably via the CT complex **a**′ with the resonance form **a** and, further, the biradical intermediate **b** produced by the addition reaction of **1** (and **2**) with a 2 M amount of TCNE. It is noteworthy that, although the reactions of the ethylene derivatives **1** and **2** with TCNE in benzene at 25 °C do not need oxygen, giving the corresponding cycloaddition products **3** and **4**, oxygen is needed for the reactions of the ethane derivatives **A** and **B** with TCNE in benzene at 25 °C, affording the corresponding cycloaddition products **C**[11] and **D**[11] (see Section 1 and Scheme 1).

3. Conclusion

We have reported the following four points in this paper: (i) reactions of the title ethylene derivatives, (*E*)-1,2-di(3-guaiazulenyl)ethylene (**1**) and 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene (**2**), with a 2 M amount of TCNE in benzene at 25 °C for 24 h under argon gave new cycloaddition compounds **3** and **4**, respectively, in 66 and 87% isolated yields; (ii) the detailed elemental and spectroscopic analyses of these products led to the molecular structures, 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene for **3** and 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene for **4**; (iii) although an X-ray crystallographic analysis of **3**, producing accurate structural parameters, has not yet been achieved because of very difficulty in obtaining a single crystal suitable for this purpose, the molecular structure of **3** established on the basis of elemental analysis and spectroscopic data could be determined by means of the X-ray diffraction; and, further, (iv) a plausible reaction pathway for the formation of the unique products **3** and **4**, possessing interesting molecular structures, was described.

4. Experimental

4.1. General

Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder, respectively. 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, respectively. NMR spectra were recorded with a JEOL GX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) at 25 °C. The ^{1}H NMR spectra were assigned using the computer-assisted simulation analysis (the 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 were measured by an ALS Model 600 electrochemical analyzer.

4.1.1. Reaction of (*E*)-1,2-di(3-guaiazulenyl)ethylene (1) with TCNE; preparation and spectroscopic properties of 1,1,2,2,11,11,12,12-octacyano-3-(3-guaiazulenyl)-8-isopropyl-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (3). To a solution of TCNE (19 mg, 148 μmol) in benzene (3 mL) was added a solution of **1** (30 mg, 71 μmol) in benzene (2 mL) under argon, turning the dark-green solution into a purple solution, rapidly. The mixture was stirred at 25 °C for 24 h under argon, gradually giving a blue precipitate of **3**, 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 dichloromethane–hexane (1/5, vol/vol) (several times) to provide pure **3** as stable crystals (32 mg, 47 μmol, 66% yield).

Compound **3**: blue prisms [$R_f = 0.39$ on silica-gel TLC (hexane/AcOEt = 7:3, vol/vol)], mp > 159 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 78.10; H, 5.38; N, 16.59%. Calcd for $C_{44}H_{36}N_8$: C, 78.08; H, 5.36; N, 16.56%; UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 246 (4.40), 296 (4.54), 308 (4.51), 357 (3.79), 373 (3.87) and 587 (2.62); IR ν_{max} (KBr) cm^{-1}, 2253 and 2249 ($-C\equiv N$); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: *m*/*z* 677.3168; calcd for $C_{44}H_{37}N_8$: $[M+H]^+$, *m*/*z* 677.3141; ^{1}H NMR (CD_2Cl_2): δ 1.140, 1.145 (3H each, d, $J = 6.9$ Hz, $(CH_3)_2CH$-8), 1.392, 1.394 (3H each, d, $J = 6.9$ Hz, $(CH_3)_2CH$-7′), 2.26 (3H, brd s, Me-5), 2.39 (3H, brd s, Me-10), 2.62 (1H, sept d, $J = 6.9$, 1.2 Hz, $(CH_3)_2CH$-8), 2.66 (3H, s, Me-1′), 3.09 (3H, s, Me-4′), 3.15 (1H, sept,

$J=6.9$ Hz, $(CH_3)_2CH$-7′), 3.76 (1H, d, $J=7.8$ Hz, H-6), 4.32 (1H, d, $J=1.4$ Hz, H-9), 4.56 (1H, brd q, H-10a), 5.708, 5.716 (0.5H each, brd d, $J=2.9$ Hz, H-3), 6.245, 6.25 (0.5H each, d, $J=2.9$ Hz, H-4), 6.35 (1H, ddd, $J=7.8$, 1.4, 1.2 Hz, H-7), 7.18 (1H, d, $J=10.9$ Hz, H-5′), 7.55 (1H, dd, $J=10.9$, 2.0 Hz, H-6′), 7.81 (1H, s, H-2′) and 8.32 (1H, d, $J=2.0$ Hz, H-8′); ^{13}C NMR (CD_2Cl_2): δ 145.5 (C-8), 143.9 (C-4′), 142.8 (C-7′), 139.8 (C-8a′), 138.2 (C-9a), 137.8 (C-2′), 135.7 (C-4b), 135.6 (C-6′), 134.9 (C-8′), 134.5 (C-10), 133.8 (C-3a′), 132.3 (C-4a), 129.8 (C-5′), 128.0 (C-5), 125.54 (C-1′), 125.51 (C-4), 122.9 (C-7), 113.8 (C-3′), 112.0 (*C*N-11), 111.8 (*C*N-12), 110.76 (*C*N), 110.73 (*C*N), 110.69 (*C*N), 110.5 (*C*N), 109.6 (*C*N-2), 108.1 (*C*N-1), 51.4 (C-10a), 49.5 (C-6), 47.3 (C-2), 45.55 (C-9), 45.51 (C-11), 44.9 (C-12), 42.8 (C-3), 42.4 (C-1), 37.5 ($(CH_3)_2CH$-7′), 34.3 ($(CH_3)_2CH$-8), 27.2 (Me-4′), 24.0, 23.9 ($(CH_3)_2$CH-7′), 23.1 (Me-5), 20.4, 19.7 ($(CH_3)_2$CH-8), 13.1 (Me-10) and 12.4 (Me-1′).

4.1.2. Reaction of 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene (2) with TCNE; preparation and spectroscopic properties of 1,1,2,2,11,11,12,12-octacyano-8-isopropyl-3,3-bis(4-methoxyphenyl)-5,10-dimethyl-1,2,3,6,9,10a-hexahydro-6,9-ethanobenz[*a*]azulene (4). To a solution of TCNE (6 mg, 47 μmol) in benzene (1 mL) was added a solution of **2** (10 mg, 23 μmol) in benzene (2 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 **4**, 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 dichloromethane–hexane (1/5, vol/vol) (several times) to provide pure **4** as stable powder (14 mg, 20 μmol, 87% yield).

Compound **4**: white powder [$R_f=0.18$ on silica-gel TLC (hexane/AcOEt=7:3, vol/vol)], mp 140 °C [decomp., determined by thermal analysis (TGA and DTA)]. Found: C, 72.71; H, 4.71; N, 15.49%. Calcd for $C_{43}H_{34}N_8O_3$ ($C_{43}H_{32}N_8O_2+H_2O$): C, 72.66; H, 4.82; N, 15.77%; UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 233 (4.45), 282 (4.24), 357 (3.14) and 410 (3.08); IR ν_{max} (KBr) cm^{-1}, 2253 and 2249 (–C≡N); exact FAB-MS (3-nitrobenzyl alcohol matrix), found: *m/z* 693.2704; calcd for $C_{43}H_{33}N_8O_2$: $[M+H]^+$, *m/z* 693.2727; ^{1}H NMR (CD_2Cl_2): δ 1.13, 1.14 (3H each, d, $J=6.9$ Hz, $(CH_3)_2$CH-8), 2.36 (3H, brd s, Me-10), 2.43 (3H, brd s, Me-5), 2.62 (1H, sept d, $J=6.9$, 0.9 Hz, $(CH_3)_2CH$-8), 3.78 (3H, s, MeO-4′), 3.83 (1H, d, $J=7.8$ Hz, H-6), 3.85 (3H, s, MeO-4″), 4.32 (1H, d, $J=1.1$ Hz, H-9), 4.40 (1H, brd q, H-10a), 6.39 (1H, ddd, $J=7.8$, 1.1, 0.9 Hz, H-7), 6.66, 6.67 (0.5H each, br d s, H-4), 6.84 (2H, dd, $J=8.5$, 2.5 Hz, H-2′,6′), 7.01 (2H, dd, $J=8.5$, 2.5 Hz, H-2″,6″), 7.39 (2H, dd, $J=8.5$, 2.5 Hz, H-3′,5′) and 7.53 (2H, dd, $J=8.5$, 2.5 Hz, H-3″,5″); ^{13}C NMR (CD_2Cl_2): δ 159.9 (C-4″), 159.6 (C-4′), 145.7 (C-8), 138.5 (C-9a), 136.1 (C-4b), 134.6 (C-10), 133.0 (C-1″), 132.2 (C-4a), 131.1 (C-3′,5′), 129.1 (C-4), 129.0 (C-1′), 128.5 (C-3″,5″), 127.9 (C-5), 122.9 (C-7), 114.2 (C-2″,6″), 113.0 (C-2′,6′), 111.9, 111.7, 111.5, 111.1 (*C*N-11 and 12), 110.7 (*C*N-1 or 2), 110.4 (2*C*N-1 or 2), 108.5 (*C*N-1), 55.7 (C-3), 55.1 (MeO-4″), 55.0 (MeO-4′), 51.5 (C-10a), 50.8 (C-2), 49.8 (C-6), 45.4 (C-9,11), 44.8 (C-12), 41.4 (C-1), 34.3 ($(CH_3)_2CH$-8), 23.6 (Me-5), 20.4, 19.7 ($(CH_3)_2$CH-8) and 13.0 (Me-10).

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References and notes

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12. The electrochemical measurement conditions of TCNE are as follows: the cyclic and differential pulse voltammograms (potential/V vs SCE) of TCNE (3 mg, 23 μmol) in 0.1 M [*n*-$Bu_4N]BF_4$, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25 °C under argon, respectively. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.45 (E_p) V by DPV and +0.42 ($E_{1/2}$, quasi-reversible) V by CV in 0.1 M [*n*-$Bu_4N]BF_4$, CH_3CN under the same electrochemical measurement conditions as TCNE.
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22. A total 10,210 reflections with $2\theta_{max} = 55.0°$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, rotating anode: 50 kV, 180 mA) at 296 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data for **3**: $C_{44}H_{36}N_8$ (FW = 676.82), blue prism (the crystal size, $0.30 \times 0.20 \times 0.30$ mm^3), monoclinic, $P2_1/n$ (#14), $a = 12.990(3)$ Å, $b = 18.635(3)$ Å, $c = 17.095(2)$ Å, $\beta = 91.72(1)°$, $V = 4136(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.087$ g/cm^3, μ(Mo Kα) = 0.66 cm^{-1}, scan width = $(1.26 + 0.30 \tan\theta)°$, scan mode = $\omega - 2\theta$, scan rate = 8.0°/min, measured reflections = 10,210, observed reflections = 9491, no. of parameters = 469, $R1 = 0.186$, $wR2 = 0.514$ and Goodness of Fit Indicator = 3.49.
23. Although the reactions of **A** and **B** with a 2 M amount of TCNE in toluene at −20 °C under argon gave the corresponding 1:2 CT complexes $\mathbf{a}_{1,2}$ (see Scheme 1),[11] respectively, in 18% isolated yield from **A** and 23% isolated yield from **B**, whose complexes were gradually converted into **C** and **D** (see Scheme 1),[11] respectively, in benzene at 25 °C under oxygen, the CT complexes **a** (see Scheme 2) have not yet been isolated because of very difficulty in obtaining the reactive CT complexes **a** produced by the reactions of **1** and **2** with a 2 M amount of TCNE in toluene at −20 °C under argon.