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New π-systems from 1-ethynylazulene

Ahmed H. M. Elwahy*

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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Abstract—A synthesis of dumbbell-shaped alkynyl-bridged diazulenyl compounds **8**, **9** as well as the triazulenylbenzene derivative **12** starting from 1-ethynyl-3-(2,3,4,5-tetraphenylphenyl)azulene (**5**) is described. © 2002 Published by Elsevier Science Ltd.

Development of conjugated oligomers and polymers has been a significant subject of many recent studies because of the numerous optical, electrochemical and electrical properties of these compounds. For this purpose, shape persistent oligomers like oligophenylene, oligo(phenylenevinylene)s and oligo(phenyleneethynylene)s appear especially attractive.[1] In particular, oligoazulenes appear to be promising candidates on account of the polarizability of the azulene system. In this respect we recently described a synthesis of mono- and polyethynylazulenes and studied their synthetic utility as building blocks for the construction of novel cyclic conjugated π-electron systems, as well as linear conjugated molecular scaffolds with ethynylazulene or butadiynylazulene units.[2] In the last decades oligo- and polyphenylene have attracted much attention since they combine the advantage of extended π-conjugation with their ability to self-assemble into various supramolecular patterns.[3] Utilizing the now available ethynylazulenes,[2] we report here the first syntheses of conjugated π-systems containing tetraphenylphenyl substituted azulenes based on the selective Diels–Alder cycloaddition between tetraphenylcyclopentadienone and ethynes.[4]

Thus, cycloaddition of an excess of tetraphenylcyclopentadienone **2** to ethynylazulenes **1a**,**b** in cyclooctane at 180°C for 12 h furnished the blue, 1-(tetraphenylphenyl)azulenes **3a**,**b** in 80 and 85% yields, respectively. The reaction proceeds via initial formation of intermediate Diels–Alder adducts that spontaneously extrude carbon monoxide to give the corresponding products **3a**,**b**.[5,6] We have also studied the alkynylation of the new azulene derivative **3a** to the corresponding ethynylated compound **5** by first reaction with one equivalent of *N*-iodosuccinimide to give the corresponding monoiodoazulene derivative **4** as green crystals (88%).[7] Cross coupling of the latter with trimethylsilylacetylene (TMSA) under Sonogashira–Hagihara[8] conditions afforded the corresponding trimethylsilyl-protected ethynylazulene, which could then be reacted with potassium hydroxide in methanol followed by chromatography on alumina (BII-III) using CH_2Cl_2/n-hexane (1:3) as eluent to give 72% of 1-ethynyl-3-(2,3,4,5-tetraphenylphenyl)azulene (**5**) as blue crystals. The new ethynylazulene **5** is reasonably stable and can be manipulated under ambient temperature. Cycloaddition of an excess of tetraphenylcyclopentadienone **2**–**5** in cyclooctane at 180°C for 12 h led to the formation of 1,3-bis(tetraphenylphenyl)azulene **6a** as blue crystals (81%). Compound **6a** was alternatively obtained in 87% yield by two-fold Diels–Alder cycloaddition of an excess of **2** to the 1,3-diethynylazulene **7a**[2] under similar conditions. Similarly, **6b** was obtained by reacting **7b**[2] with **2** (Scheme 1). The synthetic utility of the ethynylazulene **5** as a suitable building block for alkynyl-bridged tetraphenylphenylazulene systems have also been investigated (Scheme 2). Thus, the copper-mediated Eglinton[9] coupling of **5** and the palladium–copper Sonogashira[8] coupling of **5** and **4** gave rise to the dumbbell-shaped alkynyl-bridged azulenyl derivatives **8** (35%) and **9** (54%), respectively. We now extend the skeleton of **9** by inserting additional azulenylalkyne groups. Alkynes have been of interest not only as bridges but also as transmitters of π-electron resonance in novel electrophores and chromophores.[10] Thus, 2 equivalents of the ethynylazulene **5** could be coupled with 6-*tert*-butyl-1,3-diiodoazulene (**11**)[2] at room temperature in the presence of bis(triphenylphosphine)palladium(II) chloride and copper(I) iodide in triethylamine to give 41% of the corresponding trimer **10** as black crystals. The

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Keywords: Pd/Cu catalyst; cycloaddition; ethynylazulene; cobalt catalyst.

* E-mail: aelwahy@chem-sci.cairo.eun.eg

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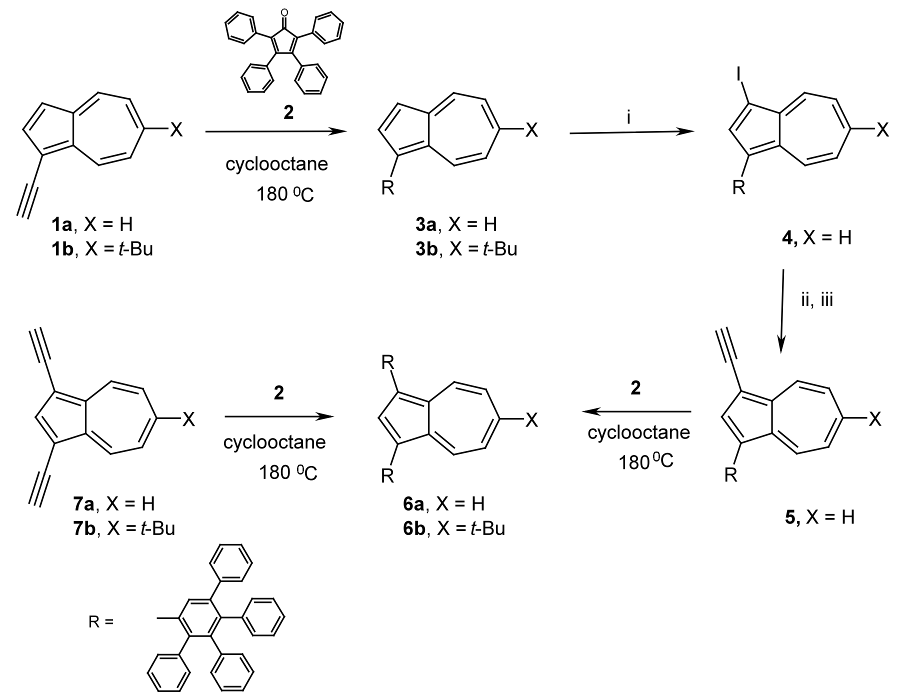
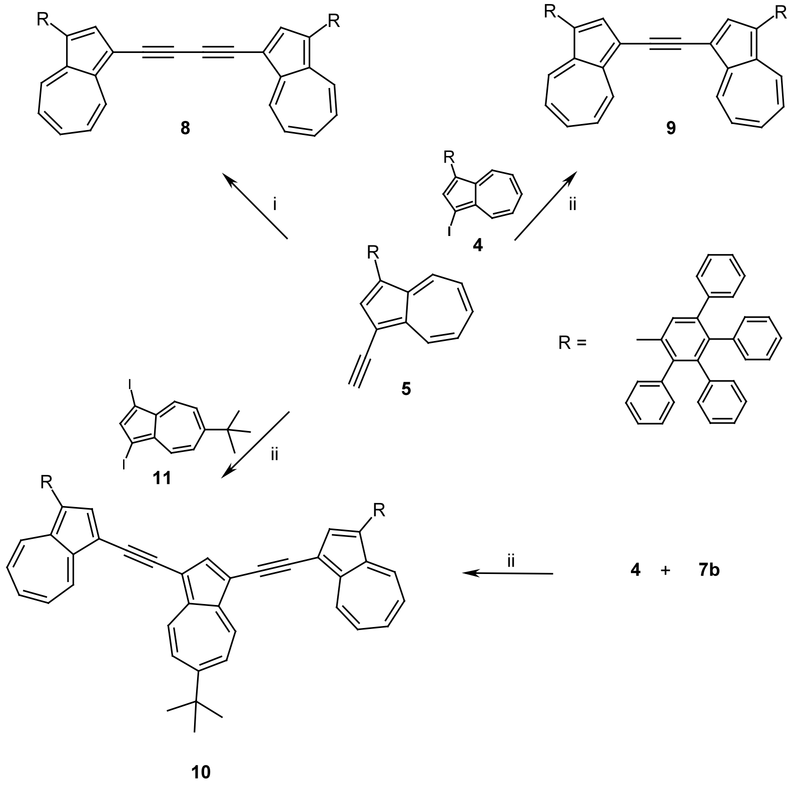


Scheme 1. *Reagents and conditions*: (i) 1 equiv. NIS, CH_2Cl_2, rt; (ii) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, 1 equiv. 1 M KOH in H_2O, MeOH, rt.



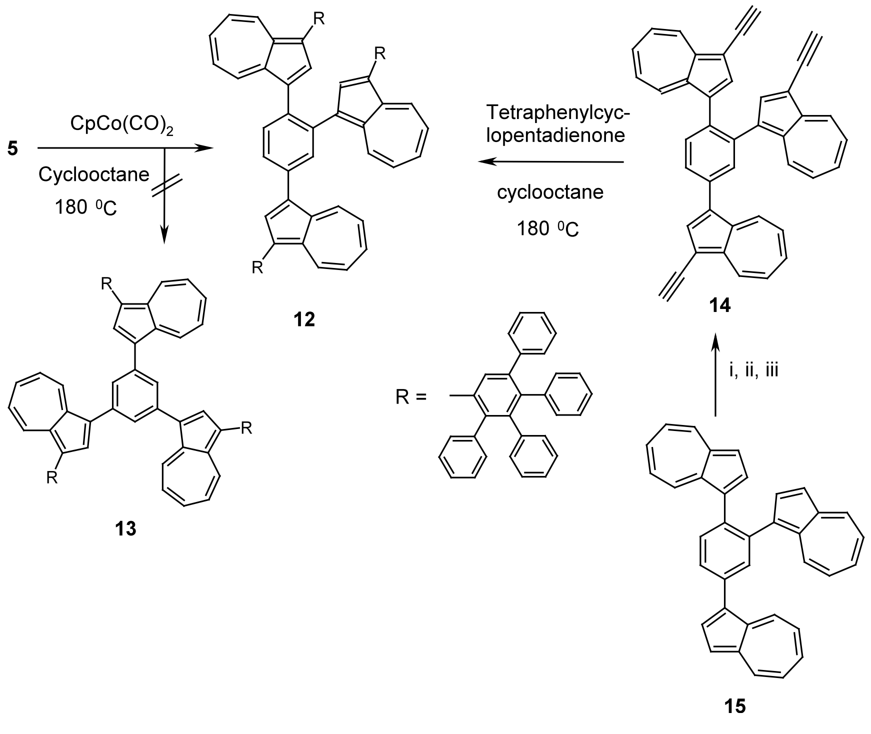
Scheme 2. *Reagents and conditions*: (i) $Cu(OAc)_2$/pyridine, 100°C; (ii) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, rt.

latter could alternatively be obtained in 44% yield by reacting 6-*tert*-butyl-1,3-diethynylazulene **7b** with iodoazulene **4** under the same conditions. The 6-*tert*-butylazulene derivatives **7b** and **11** were used to confer increased solubility to the trimers in organic solvents and thus guarantee easier processing. It was also of interest to investigate the synthetic utility of the ethynylazulene **5** as a building block for the construction of novel cyclic conjugated π-electron systems. Thus, cyclotrimerization of **5** with a catalytic amount of CpCo(CO)$_2$ in refluxing cyclooctane for 24 h furnished, after chromatography[11] of the reaction mixture, the greenish 1,2,4-[3-(2,3,4,5-tetraphenylphenyltriazulen-1-yl]benzene **12** in 10% yield (Scheme 3). The 1,3,5-triazulenylbenzene derivative **13** could not be obtained even in traces. The mechanistic explanation for the exclusive formation of **12** has been previously reported.[12] The latter was alternatively obtained in 30% yield by a three-fold Diels–Alder cycloaddition of an excess of tetraphenylcyclopentadienone (**2**) to 1,2,4-tris(3-ethynylazulene-1-yl)benzene (**14**) in cyclooctane at 180°C for 12 h. The successful synthesis of **12** from **14** provided additional proof for the structure of **12**. Compound **14** was obtained from **15**[2] by iodonation with *N*-iodosuccinimide, followed by coupling with trimethylsilylacetylene under Sonogashira conditions to give the corresponding trimethylsilyl derivative and subsequent deprotection of the trimethylsilyl group with KOH in methanol. Compounds **8**–**10** and **12** are remarkably stable showing no decomposition even after several weeks in solution or in the crystalline state.

The electronic absorption spectra of the alkynyl-bridged azulene compounds **8**–**10** (R = tetraphenylphenyl) exhibits 11, 13 and 15 nm increases, respectively, in the absorption maxima compared to the corresponding unsubstituted derivatives (**8**–**10**, R = H). Also, the triazulenylbenzene derivative **12** (R = tetraphenylphenyl) exhibits an absorption maximum at 617 nm, while that of the unsubstituted derivative **15** exhibits an absorption maximum at 600 nm.

Physical data of compounds **3b**, **4**, **5**, **6b**, **8**, **9**, **10**, **12**:[13,14]

3b: blue crystals, mp 115–117°C, MS (FD): m/z (%) 564 [M$^+$, 100%]; ^{1}H NMR: δ 1.48 (s, 9H, C(CH$_3$)$_3$), 6.87–8.55 (m, 27H, aryl H, azulenyl H); ^{13}C NMR: δ 31.77, 38.63, 116.44, 120.98, 121.50, 125.41, 125.58, 125.67, 126.29, 126.78, 126.95, 127.08, 127.72, 130.14, 130.28, 131.43, 131.70, 131.82, 132.89, 134.64, 135.30, 135.70, 136.26, 138.64, 138.72, 139.74, 140.40, 140.79, 142.04, 142.10, 161.32; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 242 (2.97) nm, 282 (2.84), 306 (2.84), 353 (2.22), 374 (2.12), 580 (4.16), 630 (sh) (4.12), 695 (sh) (3.57). **4**: green crystals, mp 136–138°C, MS (FD): m/z (%) 634 [M$^+$, 100%]; ^{1}H NMR δ 6.80–7.54 (m, 23H, aryl H, azulenyl 5/7-H), 7.63 (t, 1H, J = 9.7 Hz, azulenyl 6-H), 7.69 (s, 1H, azulenyl 2-H), 8.20 (d, 1H, J = 9.7 Hz, azulenyl 8-H), 8.40 (d, 1H, J = 9.8 Hz, azulenyl 4-H); ^{13}C NMR: δ 74.05, 123.82, 124.05, 125.49, 125.75, 126.37, 126.78, 127.03, 127.08, 127.73, 130.13, 131.08, 131.59, 131.68, 132.04, 132.81, 134.96, 153.64, 137.36, 138.64, 138.99, 139.75, 140.12, 140.25, 140.46, 140.50, 141.77, 142.01, 145.57; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 230 nm (2.94), 246 (2.99), 279 (2.79), 304 (2.76), 374 (2.10), 609 (4.20), 612 (sh) (4.13). **5**: blue crystals, mp 134–136°C, MS (FD): m/z (%) 532 [M$^+$, 100%]; ^{1}H NMR δ 3.39 (s, 1H, $\mathrm{CH{\equiv}C}$), 6.62–8.47 (m, 27H, aryl H, azulenyl H); ^{13}C NMR: δ 80.18, 81.41, 108.17, 124.31, 124.86, 125.48, 125.75, 126.37, 126.78, 127.03, 127.08, 127.73, 130.14, 131.05, 131.59, 131.69, 132.85, 135.16, 136.32, 136.70, 137.61, 138.98, 140.14, 140.25, 140.49, 141.71, 141.79, 142.00, 142.36; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 225 nm (3.33), 230 (2.96), 244 (3.02), 291 (2.8), 310 (2.8), 387 (2.17), 607 (4.19), 660 (sh) (4.12), 734 (sh) (3.63). **6b**:



Scheme 3. *Reagents and conditions*: (i) 3 equiv. NIS, CH$_2$Cl$_2$, rt; (ii) 0.04 mol% PdCl$_2$(PPh$_3$)$_2$, 0.08 mol% CuI, NEt$_3$, 3 equiv. TMSA, rt; (iii) 1.1 equiv. 1 M KOH in H$_2$O, MeOH, rt.

blue crystals, mp >250°C, MS (ESI): m/z (%) 945 [M$^+$, 100%]; ^{1}H NMR: δ 1.23 (s, 9H, C(CH$_3$)$_3$), 6.66–8.02 (m, 47H, aryl H, azulenyl H); ^{13}C NMR: δ 31.91, 38.43, 120.86, 125.37, 125.63, 126.23, 126.72, 126.86, 127.04, 127.61, 127.87, 128.19, 129.17, 129.48, 130.20, 131.42, 131.72, 131.79, 133.34, 134.94, 135.42, 136.29, 138.66, 140.22, 140.40, 140.48, 140.78, 141.67, 141.95, 161.16; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 nm (3.23), 284 (sh) (2.98), 313 (2.97), 383 (2.34), 598 (4.29), 650 (sh) (4.20), 725 (sh) (3.73). **8**: green crystals, mp 248–250°C, MS (ESI): m/z (%) 1063 [M$^+$, 100%]; ^{1}H NMR: δ 6.88–8.56 (m, 54H, aryl H, azulenyl H); UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 nm (3.68), 311 (3.47), 422 (3.05), 462 (3.0), 616 (4.28). **9**: deep green crystals, mp 223–225°C, MS (ESI): m/z (%) 1039 [M$^+$, 100%]; ^{1}H NMR: δ 6.68–8.59 (m, 54H, aryl H, azulenyl H); ^{13}C NMR: δ 90.2, 110.65, 123.78, 124.38, 125.49, 125.75, 126.38, 126.81, 127.05, 127.10, 127.75, 130.18, 130.69, 131.12, 131.66, 131.74, 133.03, 135.46, 136.58, 138.98, 140.24, 140.38, 140.50, 140.58, 140.97, 141.20, 141.86, 141.96; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 nm (3.27), 314 (3.21), 420 (2.56), 457 (2.54), 643 (4.58). **10**: black crystals, mp 238–240°C, MS (ESI): m/z (%) 1245 [M$^+$, 100%]; ^{1}H NMR: δ 1.44 (s, 9H, C(CH$_3$)$_3$), 6.76–8.54 (m, 59H, aryl H, azulenyl H); ^{13}C NMR: δ 29.83, 38.96, 89.73, 89.97, 110.57, 111.14, 123.46, 123.84, 124.41, 125.46, 125.74, 126.35, 126.77, 127.50, 127.73, 130.16, 130.69, 131.11, 131.65, 131.73, 132.99, 135.43, 136.61, 137.79, 138.97, 140.22, 140.34, 140.48, 140.56, 141.07, 141.20, 141.85, 141.96, 164.18; UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 247 nm (3.36), 279 (sh) (3.23), 311 (3.20), 329 (sh) (3.19), 333 (sh) (3.18), 419 (2.89), 640 (4.85). **12**: green crystals, mp 220–22°C, MS (ESI): m/z (%) 1598 [M$^+$, 100%]; ^{1}H NMR: δ 6.51–8.50 (m, 84H, aryl H, azulenyl H); UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 nm (3.35), 308 (3.14), 383 (2.5), 618 (4.48), 675 (sh) (4.38).

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13. All new compounds described gave correct elemental analyses.
14. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in CDCl$_3$ with tetramethylsilane as internal standard. UV–vis spectra were recorded with a Perkin Elmer Lambda 20 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument.