

118. Syntheses and Properties of Donor/Acceptor Arylethynyl-Substituted 1,6-Methano[10]annulenes

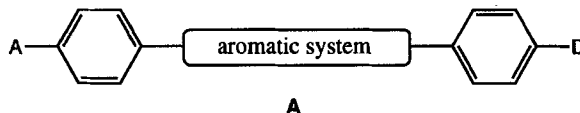
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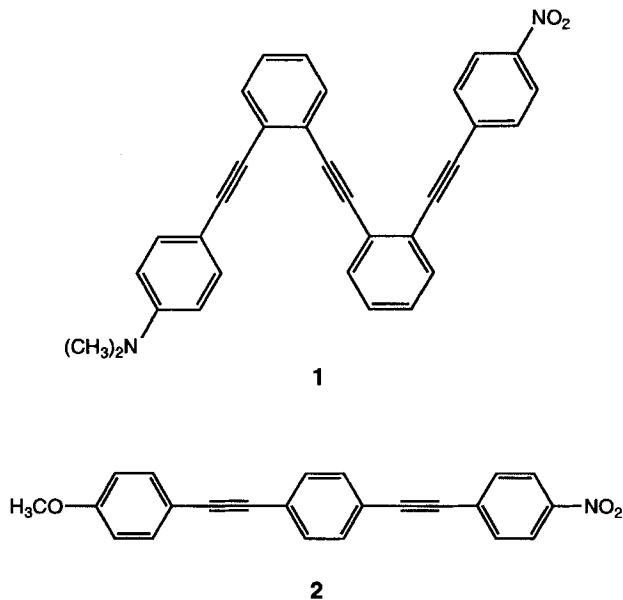
The stepwise palladium-catalyzed coupling of dibromo-1,6-methano[10]annulene derivatives to a phenylacetylene substituted by an electron-withdrawing group followed by coupling with a phenylacetylene possessing an electron-donating group allows the preparation of donor/acceptor systems which contain three aromatic moieties linked by ethynediyl bridges. The same type of cross-coupling starting from 2-ethynyl-1,6-methano[10]annulene and bromo-substituted azobenzene derivatives provides easy access to a new class of azo dyes. The properties of these compounds are compared to those of analogous compounds containing only benzene rings.

Introduction. – Recently, we described the syntheses of thio-substituted 1,6-methano[10]annulenes which were incorporated into ethynediyl-connected benzene/annulene donor/acceptor systems [1]. The UV/VIS spectra of these compounds showed absorbances similar to those found in benzene/benzeneethynediyl-connected donor/acceptor system [2]. The successful synthesis of donor/acceptor (phenylethynyl)-1,6-methano[10]annulenes, triggered our search for other donor/acceptor molecules containing ethynyl-1,6-methano[10]annulene moieties. From the many different types encountered in the literature, a system containing at least three aromatic moieties connected by ethynediyl bridges (see **A**) was chosen for our purposes. In molecules of this type, two aromatic rings bearing the donor (D) and acceptor (A) groups are interconnected by various aromatic moieties such as benzene, naphthalene, or anthracene.



Many research groups have synthesized complex aromatic compounds which contain electron-donating and electron-accepting substituents as possible substrates for nonlinear optics or liquid crystals [3]. One type which has received a great deal of attention and is a representative of the system denoted in **A** is the compound class of PPE's or poly(phenyleneethynyls). Some of these compounds have been shown to possess high thermal stability, nonlinear optical properties, and liquid-crystal properties [4]. Typical examples are 1,4-bis(phenylethynyl)benzenes and 9,10-bis(phenylethynyl)anthracenes. Derivatives of **1** and **2** are usually obtained *via* palladium-catalyzed coupling of a terminal acetylene to an aromatic halide. Due to our successful use of bromo-substituted

1,6-methano[10]annulenes in palladium-catalyzed cross-coupling reactions [1] [5], we decided to use the annulene ring as the central aromatic core of such a donor/acceptor system.



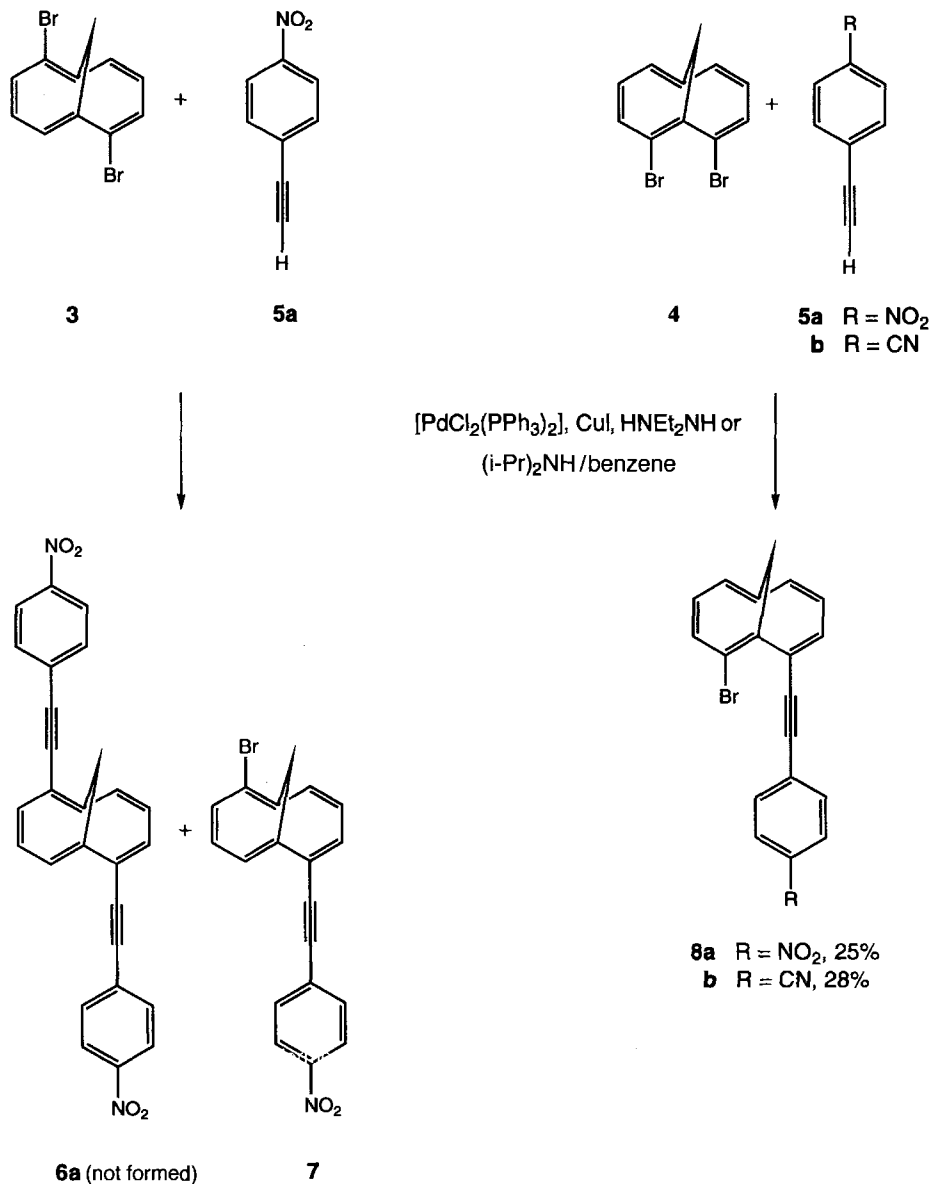
Following this same line of thought, we decided also to incorporate the ethynyl-1,6-methano[10]annulene moiety into compounds containing azobenzene fragments. In this case, the 1,6-methano[10]annulene ring is connected to an azobenzene derivative *via* an ethynediyl bridge. The second ethynediyl bridge in the above described group of compounds is replaced by an azo group. Similar substances in which a phenylethynyl substituent is connected to a substituted azobenzene were reported in 1993 by *Boldt* and coworkers [6]. These compounds which were obtained *via* palladium-catalyzed coupling of a terminal acetylene to the halogeno-substituted azobenzene derivative were synthesized as potential substrates for molecular switches.

Results and Discussion. – The easily obtainable 2,7- and 2,10-dibromo-1,6-methano[10]annulenes (**3** and **4** resp.) were chosen as coupling partners for phenylacetylenes substituted in the *para*-position with electron-withdrawing groups. The initial coupling of an electron-poor acetylene to the annulene system followed by coupling of the electron-rich acetylene was chosen since literature precedent have shown that the yields are usually poor or the reaction does not proceed at all when the synthesis is carried out in the reverse manner [7]. The acetylenes chosen for this purpose were the *para*-nitro- and *para*-cyano-substituted phenylacetylene **5a** and **5b**, respectively.

We thought it would be interesting to study the properties of a diacceptor-substituted derivative as compared to one substituted with a donor- and an acceptor-substituted phenylacetylene unit. However, in attempts to synthesize such a compound **6a** from 2,7-dibromo-1,6-methano[10]annulene (**3**) and **5a** using $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI as catalyst in Et_2NH (*Scheme 1*), we were unable to isolate any of the desired material.

The starting material (70%) was isolated along with the monoalkynylated derivative **7** and a compound believed to be a naphthalene derivative which resulted from the reaction of the solvent with the dimer of **5a**. Since butadiynes are often reported as by-products in such coupling reactions, this possibility seems quite feasible [8]. Neither the mechanism of formation of this compound nor the absolute structure have been completely resolved. Because this reaction sequence could not be optimized, it was abandoned.

Scheme 1



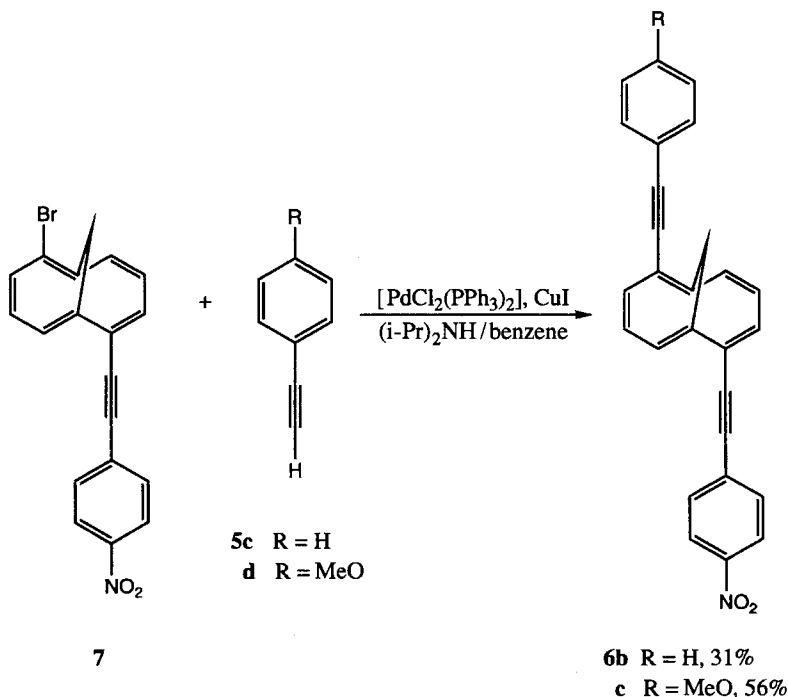
At this point, we concentrated on the synthesis of the monoalkynylated derivatives needed for the coupling to donor-substituted acetylenes. Nitro-substituted derivative **7** was obtained in 33% yield by coupling of 1.2 equiv. of **5a** with **3** using 5 mol-% of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in Et_2NH ; when more **5a** was used, the yields of **7** were considerably lower (Scheme 1). The analogous reaction using the *para*-cyano-substituted phenylacetylene **5b** and **3** was not successful.

Under slightly different reaction conditions, 2 mol-% of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and 1 mol-% of CuI in benzene/ $(i\text{-Pr})_2\text{NH}$ 10:2, the 2,10-disubstituted derivatives **8a** and **8b** were obtained in 25 and 28% yield from **4** and **5a** or **5b**, respectively. Extensive studies were carried out varying catalysts, catalyst amounts, and solvents in attempts to increase the yield, but all experiments performed were unsuccessful.

With the monoalkynylated derivatives **7** and **8** in hand, we turned to the synthesis of our target molecules, the donor/acceptor-substituted compounds. To find the most effective reaction conditions for the coupling of unsubstituted and *para*-methoxy-substituted phenylacetylenes **5c** and **5d**, respectively, with our monoalkynylated compounds (Scheme 2), a variety of reactions conditions were tested. In the synthesis of the 2,7-disubstituted derivatives **6b** and **6c** the best results were obtained when the reaction of **7** with **5c, d** was carried out in the presence of the usual catalyst system $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI in benzene/ $(i\text{-Pr})_2\text{NH}$ 1:1; yielding the products as bright yellow crystals.

The synthesis of 2,10-disubstituted derivatives was attempted in view of the investigation of through-space interactions between donor and acceptor substituents. How-

Scheme 2

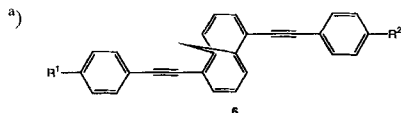


ever, the couplings of compounds **8a** and **8b** with phenylacetylenes **5c** or **5d** were unsuccessful, probably due to steric hindrance at the reaction site.

Donor/acceptor-substituted acetylenes are expected to exhibit at least two different types of bands in the UV/VIS spectrum: broad low-energy bands are usually indicative of intramolecular charge transfer and sharper higher-energy bands of $\pi-\pi^*$ transitions [2]. The UV/VIS data of compounds **6b** and **6c** were compared with those of the unsubstituted parent **6d** and of the benzene analogue **2** (see *Table*). In the spectrum of the neither donor- nor acceptor-substituted **6d**, the band at 376 nm is likely to result from a $\pi-\pi^*$ transition and that at 271 nm from transitions within the phenylacetylene part of the molecule; a band at 268 nm of 1-(phenylethynyl)naphthalene is assigned to such a transition [9]. The other bands of **6d** can be assigned to transitions involving the annulene ring and the phenyl substituent.

Table. UV/VIS Data of Substituted 2,7-Diethynyl-1,6-methano[10]annulenes **6b–d** and 1,4-Diethynylbenzene **2**

| | R ¹ | R ² | λ_{\max} (lg ϵ) | | R ¹ | R ² | λ_{\max} (lg ϵ) |
|-------------------------|----------------|-----------------|-----------------------------------|-------------------------|----------------|-----------------|-----------------------------------|
| 6b ^{a)} | H | NO ₂ | 258 (3.13) | 6d ^{a)} | H | H | 238 (4.30) |
| | | | 282 (4.54) | | | | 271 (4.58) |
| | | | 392 (4.45) | | | | 280 (4.59) |
| 6c ^{a)} | MeO | NO ₂ | 281 (4.60) | 2 ^{b)} | MeO | NO ₂ | 294 (4.51) |
| | | | 357 (4.30) | | | | 356 (4.57) |
| | | | 398 (4.48) | | | | |

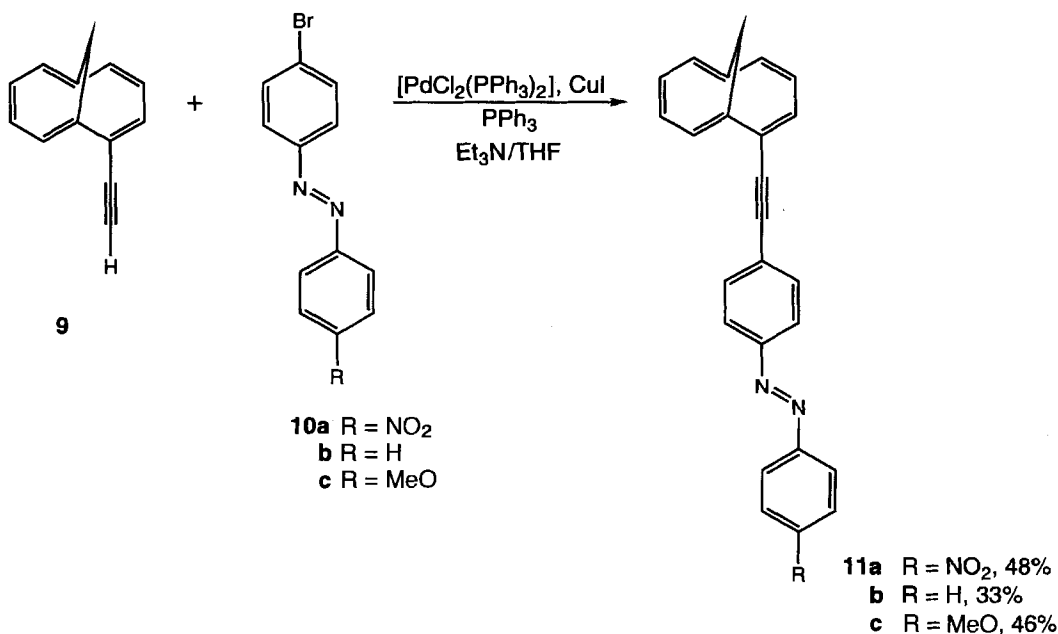


b) The central methano[10]annulene moiety of **6** is replaced by a benzene moiety.

Most interesting is the comparison of the spectra of compounds **2** and **6c**. Even though the central benzene ring is replaced by a 1,6-methano[10]annulene ring, the absorption spectra of both **2** and **6c** show two bands with similar absorbances and extinction coefficients. This comparison is relevant due to the fact that compound **2** has been shown to display interesting nonlinear optical properties [2].

As an extension of this topic, 4-[(1,6-methano[10]annulen-2-yl)ethynyl]azobenzenes were investigated. The method developed by *Boldt* and coworkers [6] for the synthesis of 4-(phenylethynyl)azobenzenes was utilized for the synthesis of these target molecules, which required as starting materials 2-ethynyl-1,6-methano[10]annulene (**9**) and several bromo-substituted azobenzenes, e.g., **10a–c** (see *Scheme 3*). Ethynylmethano[10]annulene **9** was synthesized from 2-bromo-1,6-methano[10]annulene and (trimethylsilyl)acetylene by palladium-catalyzed coupling [10]. The resulting trimethylsilyl-protected acetylene was then deprotected by treatment with base (KOH in EtOH). The bromo-azobenzenes were obtained *via* standard azo coupling or *via* the reaction of an aryl nitroso compound with an aryl amine. The annulene component **9** was then coupled to the azobenzene **10** using a catalyst system consisting of [PdCl₂(PPh₃)₂]/CuI/PPh₃ in THF/Et₃N. The 4-[(1,6-methano[10]annulen-2-yl)azobenzenes **11a–c** were obtained in 48, 33, and 46% yield, respectively.

Scheme 3



The UV/VIS spectra of the azobenzenes **11 a–c** reflect the influence of the corresponding *para*-substituent. The absorptions at longest wavelengths are assigned to the π – π^* ($\lg \epsilon > 4$) transitions [6], *i.e.*, the bands at 372 nm for **11 b** and **11 c** and at 408 nm for **11 a**. Thus, the replacement of a H-atom (**10 b**) by the electron-donating MeO group (**11 c**) has no effect on the π – π^* transition, whereas replacement by a NO₂ substituent (**11 a**) produces a bathochrom shift of 26 nm. These values are in good agreement with the absorbances found in the UV/VIS spectra of compounds in which the 1,6-methano-[10]annulene moiety is replaced by a benzene ring [6].

Conclusion. – Our results show that the synthesis of ethynyl-1,6-methano[10]annulenes *via* palladium-catalyzed coupling reactions can be extended to the synthesis of several different classes of alkynyl compounds. The stepwise cross-coupling makes symmetrically and unsymmetrically substituted systems available. The coupling can be conducted in a manner which allows the isolation of the monoalkynylated intermediates which can be coupled to a variety of differently substituted acetylenes. An extension of this methodology also proved to be useful for the synthesis of new azo dyes. The above mentioned stepwise cross-coupling with donor- and acceptor-substituted 4-ethynyl-azobenzene derivatives could be useful in the synthesis of 1,6-methano[10]annulene derivatives which possess a donor/acceptor system consisting of multiple azobenzene substituents.

We would like to thank *BASF AG*, *Bayer AG*, and *Hoechst AG*, the *Verband der Chemischen Industrie*, *Fonds der Chemie*, as well as the *Deutsche Forschungsgemeinschaft* for support of this work, *Hewlett-Packard* and *Varian* for providing UV/VIS spectrometers, Ms. *U. Hertle* and Dr. *W. Kramer* for NMR measurements, and Mr. *H. Rudy* and Mr. *P. Weyrich* for mass spectra and elemental analyses.

Experimental Part

General. See [1].

2-Bromo-7-[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (7). To a deoxygenated soln. of 2,7-dibromo-1,6-methano[10]annulene (**3**; 300 mg, 1.00 mmol) in Et₃N (10 ml), [PdCl₂(PPh₃)₂] (35 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), and 1-ethynyl-4-nitrobenzene (**5a**; 177 mg, 1.20 mmol) were added. The mixture was stirred overnight at 25°, the solvent removed, and the residue adsorbed on *Celite*. CC (silica gel) with hexane as eluent yielded starting **3** (67%) and with hexane/AcOEt acetate 100:1 119 mg (33%) of **7**. M.p. 140–143°. UV/VIS (hexane): 373 (4.34), 353 (4.32), 243 (4.03), 278 (4.45). IR (KBr): 3008m, 2943m, 2881m, 2471m, 2219w, 1562m, 1462s, 1399s, 1310m, 1298m, 1276m, 1150m, 1059m, 965w, 950m, 775m, 756s, 732m, 678m. ¹H-NMR (300 MHz, CDCl₃): 8.24 (*dt*, ³*J* = 9, ⁴*J* = 2.1, 2H_m to C≡C); 7.79, 7.78 (*2d*, ³*J* = 9, ⁴*J* = 2.1, H–C(5), H–C(10)); 7.68 (*dt*, ³*J* = 9.3, ⁴*J* = 2.1, 2H_e to C≡C); 7.56, 7.41 (*2d*, ³*J* = 9.6, 9.9 each, 1H, H–C(3), H–C(8)); 7.26, 7.14 (*t*, ³*J* = 9.3, *dd*, ³*J* = 9, each 1H, H–C(4), H–C(9)); –0.13 (*t*, 2H–C(11)). ¹³C-NMR (75 MHz, CDCl₃): 146.8 (C_p to C≡C); 130.0 (C_{ipso} to C≡C); 132.9, 132.4, 132.1, 130.2, 139.0, 128.4, 127.8 (arom. CH); 123.5 (C_m to C≡C); 121.1 (C(7)); 118.8, 118.0, 113.5 (C(1), C(6), C(2)); 92.2, 91.2 (C≡C); 34.4 (C(11)). EI-MS (158°): 367 (27, [M (⁸¹Br)]⁺), 365 (28, [M (⁷⁹Br)]⁺), 286 (37, [M – Br]⁺), 239 (100, [M – C₆H₄NO₂]⁺). HR-MS: 365.0050 (C₂₀H₁₂BrNO₂⁺; calc. 366.0050).

4-(10-Bromobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-2-yl)benzotrile (8b). To a deoxygenated soln. of 2,10-dibromo-1,6-methano[10]annulene (**4**; 300 mg, 1.00 mmol) in (i-Pr)₂NH (2 ml) and benzene (10 ml) [PdCl₂(PPh₃)₂] (14 mg, 0.02 mmol) and CuI (1 mg, 0.01 mmol) were added. After stirring for 10 min, 4-ethynylbenzotrile (**5b**; 153 mg, 1.20 mmol) was added. The mixture was stirred overnight at 80°, then cooled to r.t., and evaporated and the residue adsorbed on *Celite*. CC (silica gel, hexane) gave starting **4** (52%), followed by **8b** (97 mg, 28%). Yellow crystals. M.p. 124–125°. UV/VIS (hexane): 361 (4.17), 285 (4.34), 244 (4.06). IR (KBr): 3042m, 2949m, 2225s, 2201s, 1917w, 1724w, 1668w, 1602s, 1498m, 1447m, 1414m, 1405m, 1307m, 1321m, 1321m, 1265m, 1221m, 1171m, 1115m, 1105m, 1013m, 964w, 918m, 896s, 837s, 781s, 766m. ¹H-NMR (300 MHz, CDCl₃): 7.62 (*s*, C₆H₄CN); 7.59, 7.53, 7.48, 7.47 (*2d*, each ³*J* = 9.9 and 1H, *m*, 2H, H–C(3), H–C(5), H–C(7), H–C(9)); 7.20, 7.09 (*t*, ³*J* = 9.2, *dd*, ³*J* = 8.6, each 1H, H–C(4), H–C(8)); –0.26 (*dd*, ²*J* = 10.5, ⁴*J* = 0.9, H_a–C(11)); –0.33 (*dd*, ²*J* = 10.4, ⁴*J* = 1.1, H_b–C(11)). ¹³C-NMR (75 MHz, CDCl₃): 135.2, 132.6, 132.1, 131.5, 131.2, 129.3, 128.7, 128.0 (arom. C–H); 122.8, 122.1 (C(2), C_p to CN); 118.6, 117.8, 117.4 (C(1), C(6), CN); 111.3, 110.2 (C(10), C_{ipso} to CN); 94.3, 94.2 (C≡C); 35.2 (C(11)). EI-MS (152°): 347 (29, [M (⁸¹Br)]⁺), 345 (33, [M (⁷⁹Br)]⁺), 266 (100, [M – Br]⁺), 240 (10, [M – Br – CN]⁺). HR-MS: 345.0155 (C₂₀H₁₂BrN⁺; calc. 345.0153). Anal. calc. for C₂₀H₁₂BrN: C 69.38, H 3.49, N 4.05; found: C 69.08, H 3.72, N 4.10.

2-Bromo-10-[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (8a). To a deoxygenated soln. of **4** (264 mg, 0.88 mmol) in (i-Pr)₂NH (2 ml) and benzene (10 ml), [PdCl₂(PPh₃)₂] (14 mg, 0.02 mmol) and CuI (1 mg, 0.01 mmol) were added. To this soln. was then added **5a** (162 mg, 1.1 mmol). The mixture did not become a soln. until a reaction temp. of 80° was reached. After stirring overnight at 80°, the soln. was cooled to r.t. and evaporated and the residue adsorbed on *Celite*. CC (silica gel, hexane) gave first starting **4** (15%) and then **8a** (79 mg, 25%). Yellow crystals. M.p. 187–189°. UV/VIS (hexane): 379 (4.27), 357 (4.26), 284 (4.33), 256 (sh. 4.01), 248 (4.23). IR (KBr): 2924m, 2854m, 2191w, 1590m, 1559m, 1512s, 1490m, 1457m, 1335s, 1265m, 1104m, 1058m, 960w, 850m, 780m, 748m. ¹H-NMR (300 MHz, CDCl₂): 8.23 (*dt*, ³*J* = 8.7, ⁴*J* = 1.8, 2H_m to C≡C); 7.70 (*dt*, ³*J* = 8.7, ⁴*J* = 1.8, 2H_e to C≡C); 7.62, 7.51 (*2d*, ³*J* = 9.6, 10.2, each 1H, H–C(3), H–C(9)); 7.56, 7.49 (*dd*, ³*J* = 8.7, ³*J* = 8.4, each 1H, H–C(7), H–C(5)); 7.23, 7.12 (*t*, ³*J* = 9.5, *dd*, ³*J* = 8.7, each 1H, H–C(4), H–C(8)); –0.27 (*dd*, ²*J* = 11.4, 2H–C(11)). ¹³C-NMR (75 MHz, CDCl₃): 146.7 (C_p to C≡C); 130.6 (C_{ipso} to C≡C); 135.1, 132.5, 131.5, 131.1, 129.1, 128.5, 127.8 (arom. CH); 123.5 (C_m to C≡C); 122.5, 121.9, 117.3, 110.1 (C(1), C(2), C(6), C(10)); 95.0, 94.0 (C≡C); 35.2 (C(11)). EI-MS (147°): 367 (24, [M (⁸¹Br)]⁺), 365 (26, [M (⁷⁹Br)]⁺), 286 (25, [M – Br]⁺), 239 (100, [M – C₆H₄NO₂]⁺). HR-MS: 365.0050 (C₁₉H₁₂BrNO₂⁺; calc. 365.0050).

2,7-Bis(phenylethynyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (6d). To a deoxygenated soln. of **3** (300 mg, 1 mmol), [PdCl₂(PPh₃)₂] (35 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added. The mixture was stirred for 10 min, then ethynylbenzene (**5c**; 245 mg, 2.40 mmol) was added. After 5 h stirring at r.t., the solvent was evaporated and the remaining residue adsorbed on *Celite* and submitted to CC (silica gel, hexane): **6d** (342 mg, 92%). Deep yellow oil. UV/VIS (hexane): 238 (4.30), 271 (4.58), 280 (4.59), 376 (4.42). IR (film): 3014w, 2879m, 2350w, 1573m, 1446m, 1359w, 1311w, 1279w, 1224w, 1186w, 1164w, 1134w, 1073m, 1032w, 1025m, 1007m, 1001m, 974w, 810m, 792w, 751m, 742m, 713w, 705w, 396m, 621w. ¹H-NMR (300 MHz, CDCl₃): 7.84 (*d*, ³*J* = 8.7, H–C(5), H–(10)); 7.57 (*m*, 4H_e to C≡C); 7.48 (*d*, ³*J* = 9.6, H–C(3), H–(8)); 7.35 (*m*, 4H_m to C≡C, 2H_p to C≡C); 7.19 (*t*, ³*J* = 9, H–C(4), H–C(9)); –0.15 (*s*, 2H–C(11)). ¹³C-NMR (75 MHz, CDCl₃): 131.9, 131.4, 129.8, 128.3, 128.2, 128.2, 127.3 (arom. CH); 123.2, 122.0 (C(2), C(7), C_{ipso} to C≡C); 117.9 (C(1), C(6)); 93.0,

87.2 (C≡C); 35.0 (C(11)). EI-MS (172°): 344 (4), 343 (27), 342 (100, M^+), 341 (64), 340 (18), 339 (34), 338 (7), 337 (14), 266 (9), 265 (37, $[M - \text{Ph}]^+$), 264 (10), 263 (21), 77 (3). HR-MS: 342.1409 ($\text{C}_{27}\text{H}_{18}^+$; calc. 342.1409).

2-[(4-Nitrophenyl)ethynyl]-7-(phenylethynyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**6b**). To a deoxygenated soln. of **7** (100 mg, 0.27 mmol) in Et_2NH (3 ml) and benzene (2 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (10 mg, 0.01 mmol) and CuI (3 mg, 0.01 mmol) were added. The mixture was stirred 10 min, and then **5c** (33 mg, 0.33 mmol) was added. The soln. was stirred overnight and then evaporated and the remaining residue adsorbed on *Celite*. CC (silica gel, hexane) and recrystallization from $\text{MeOH}/\text{CH}_2\text{Cl}_2$ yielded **6b** (32 mg, 31%). Orange crystals. M.p. 160–161°. UV/VIS (hexane): 392 (4.45), 282 (4.54), 258 (3.1). IR (film): 3014 w , 2879 m , 2350 w , 1573 m , 1446 m , 1359 w , 1311 w , 1279 w , 1224 w , 1186 w , 1164 w , 1134 w , 1073 m , 1032 w , 1025 m , 1007 m , 1001 m , 974 w , 810 m , 792 w , 751 m , 742 m , 713 w , 705 w , 696 m , 621 w . $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.23 (*dt*, $^3J = 9$, $^4J = 2.1$, 2 H_m to $\text{C}\equiv\text{C}-\text{C}(2)$); 7.79, 7.80 (*2d*, $^3J = 8.7$, *d*, $^3J = 9$, each 1 H, $\text{H}-\text{C}(5)$, $\text{H}-\text{C}(10)$); 7.68 (*dt*, $^3J = 9.0$, $^4J = 2.1$, 2 H_o to $\text{C}\equiv\text{C}-\text{C}(2)$); 7.57 (*m*, 2 H_o to $\text{C}\equiv\text{C}-\text{C}(7)$); 7.52, 7.49 (*2d*, $^3J = 5.1$, 5.4, each 1 H, $\text{H}-\text{C}(3)$, $\text{H}-\text{C}(8)$); 7.38 (*m*, 2 H_m to $\text{C}\equiv\text{C}-\text{C}(7)$, H_p to $\text{C}\equiv\text{C}-\text{C}(7)$); 7.23 (*t*, $\text{H}-\text{C}(4)$, $\text{H}-\text{C}(9)$); -0.09 (*dd*, $^2J = 10$, $^4J = 0.9$, $\text{H}_a-\text{C}(11)$); -0.16 (*dd*, $^2J = 9.6$, $^4J = 1.2$, $\text{H}_b-\text{C}(11)$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 146.7 (C_p to $\text{C}\equiv\text{C}-\text{C}(2)$); 130.1 (C_{ipso} to $\text{C}\equiv\text{C}-\text{C}(2)$); 132.4, 132.0, 132.0, 131.0, 131.4, 130.8, 129.4, 128.2, 127.7, 127.3 (arom. CH); 123.0, 122.4, 120.5 (C(2), C(7)), C_{ipso} to $\text{C}\equiv\text{C}-\text{C}(7)$); 117.9, 117.8 (C(1), C(6)); 93.3, 92.7, 91.1, 86.9 (2 C≡C); 35.0 (C(11)). EI-MS (177°): 388 (28), 387 (100, M^+), 386 (27), 341 (24, $[M - \text{NO}_2]^+$), 340 (47), 339 (57), 338 (17), 337 (29), 326 (18), 265 (21, $[M - \text{C}_6\text{H}_4\text{NO}_2]^+$), 264 (15), 263 (28), 239 (6), 170 (6), 77 (2). HR-MS: 387.1258 ($\text{C}_{27}\text{H}_{17}\text{NO}_2^+$; calc. 387.1258).

2-[(4-Methoxyphenyl)ethynyl]-7-[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**6c**). To a deoxygenated soln. of **7** (102 mg, 0.28 mmol) in (*i*-Pr) $_2\text{NH}$ (5 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (6 mg, 2 mol-%, 0.01 mmol) and CuI (2 mg, 2 mol-%, 0.01 mmol), and after stirring for 10 min, 1-ethynyl-4-methoxybenzene (**5d**; 214 mg, 1.62 mmol) were added. The mixture was stirred overnight at 80°, cooled to r.t., and evaporated and the residue adsorbed on *Celite*. CC (silica gel, hexane) gave **6c** (66 mg, 56%). Bright yellow crystals. M.p. 156–159°. UV/VIS (hexane): 281 (4.60), 357 (4.30), 398 (4.48). IR (KBr): 2933 w , 2839 w , 2198 m , 2137 w , 1592 s , 1562 m , 1506 s , 1463 m , 1374 w , 1347 s , 1305 m , 1295 m , 1254 s , 1180 m , 1168 s , 1107 m , 1026 s , 839 s , 820 s , 784 m , 770 m , 757 s , 749 m , 687 m , 613 w , 558 w , 537 w , 493 w . $^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.22 (*dt*, $^3J = 9$, $^4J = 2.1$, 2 H_m to $\text{C}\equiv\text{C}-\text{C}(7)$); 7.89, 7.78 (*2d*, each $^3J = 8.7$ and 1 H, $\text{H}-\text{C}(5)$, $\text{H}-\text{C}(10)$); 7.67 (*dt*, $^3J = 9$, 2 H_o to $\text{C}\equiv\text{C}-\text{C}(7)$); 7.49 (*m*, $\text{H}-\text{C}(3)$, $\text{H}-\text{C}(8)$, 2 H_m to $\text{C}\equiv\text{C}-\text{C}(2)$); 7.22 (*t*, $\text{H}-\text{C}(4)$, $\text{H}-\text{C}(9)$); 6.90 (*dt*, $^3J = 6.75$, $^4J = 2.4$, 2 H_a to $\text{C}\equiv\text{C}-\text{C}(2)$); 3.83 (*s*, MeO); -0.07 (*m*, 2 $\text{H}-\text{C}(11)$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 159.7 (C_p to $\text{C}\equiv\text{C}-\text{C}(2)$); 146.7 (C_p to $\text{C}\equiv\text{C}-\text{C}(7)$); 133.9, 133.0, 132.4, 131.90, 131.8, 130.9, 129.1, 127.8, 127.2, 123.6 (arom. CH); 130.02 (C_{ipso} to $\text{C}\equiv\text{C}-\text{C}(7)$); 123.0, (C(7)); 120.4 (C(2)); 118.0, 117.9, 115.2 (C(1), C(6)), C_{ipso} to $\text{C}\equiv\text{C}-\text{C}(2)$); 114.0 (C_o to $\text{C}\equiv\text{C}-\text{C}(2)$); 93.5, 92.8, 91.2, 85.8 (2 C≡C); 55.3 (MeO); 35.0 (C(11)). EI-MS (216°): 417 (100, M^+), 402 (8, $[M - \text{Me}]^+$), 386 (8, $[M - \text{MeO}]^+$). HR-MS: 417.1367 ($\text{C}_{28}\text{H}_{17}\text{NO}_3^+$; calc. 417.1367).

Azo Compounds: General Procedure. To a deoxygenated soln. of 2-ethynyl-1,6-methano[10]annulene (**9**; 125 mg, 0.75 mmol) in Et_3N (10 ml) and THF (10 ml), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (11 mg, 2 mol-%, 0.02 mmol), CuI (1 mg, 1 mol-%, 0.01 mmol), and PPh_3 (20 mg, 10 mol-%, 0.08 mmol) were added. The yellow soln. was stirred for 10 min at r.t. Then the azobenzene derivative (0.75 mmol) was added (\rightarrow color of the azobenzene derivative). This mixture was stirred overnight at 80°, cooled to r.t., and evaporated. The resulting solid was dissolved in as little CH_2Cl_2 as possible, adsorbed on *Celite*, and submitted to CC.

4-[(Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-2-yl)ethynyl]phenyl]phenyldiazene (**11b**): From 4-bromoazobenzene (**10b**; 196 mg, 0.75 mmol). CC (silica gel, hexane/AcOEt 100:1) gave 85 mg (33%) of **11b**. Golden crystals. M.p. 119–120°. UV/VIS (CH_2Cl_2): 372 (4.50), 262 (4.62). IR (KBr): 3090 m , 2938 m , 1700 w , 1653 w , 1594 w , 1440 w , 1249 m , 1100 w , 849 s , 820 m , 765 s , 725 s , 687 s , 623 s , 560 s , 511 m , 473 m , 419 m , 410 m . $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.93 (*dt*, $^3J = 8.1$, $^4J = 1.8$, 2 H_m to $\text{C}\equiv\text{C}$, 2 H_o of Ph); 7.88 (*m*, $\text{H}-\text{C}(10)$); 7.69 (*dd*, $^3J = 9$, 2 H_o to $\text{C}\equiv\text{C}$); 7.49 (*m*, 2 H_m of Ph, H_p of Ph, $\text{H}-\text{C}(3)$, $\text{H}-\text{C}(5)$, $\text{H}-\text{C}(7)$); 7.21 (*m*, $\text{H}-\text{C}(8)$, $\text{H}-\text{C}(9)$); 7.11 (*t*, $^3J = 9$, $\text{H}-\text{C}(4)$); -0.20 (*d*, $^2J = 9.3$, $\text{H}_a-\text{C}(11)$); -0.37 (*dd*, $^2J = 9.3$, $^4J = 0.9$, $\text{H}_b-\text{C}(11)$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 152.4, 151.4 (C_p to $\text{C}\equiv\text{C}$, C_{ipso} of Ph); 132.0, 131.2, 131.0, 130.0, 128.9, 128.7, 128.6, 128.3, 127.3, 127.1, 126.2, 122.8, 122.7 (arom. CH); 126.1 (C_{ipso} to $\text{C}\equiv\text{C}$); 121.7 (C(2)); 116.8, 115.6 (C(1), C(6)); 92.3, 90.1 (C≡C); 34.9 (C(11)). EI-MS (134°): 346 (76, M^+), 241 (100, $[M - \text{N}_2\text{Ph}]^+$). HR-MS: 346.1471 ($\text{C}_{25}\text{H}_{18}\text{N}_2$; calc. 346.1470).

4-[(Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-2-yl)ethynyl]phenyl] (4-methoxyphenyl)diazene (**11c**): From 4-bromo-4'-methoxyazobenzene (**10c**; 218 mg, 0.75 mmol). CC (silica gel, hexane/AcOEt 100:1) gave 130 mg (46%) of **11c**. Orange red crystals. M.p. 102–103°. UV/VIS (CH_2Cl_2): 372 (4.45), 262 (4.56). IR (KBr): 2943 w , 2836 m , 2192 w , 1601 s , 1583 w , 1529 w , 1497 s , 1463 m , 1440 m , 1415 m , 1401 m , 1320 m , 1296 m , 1251 s , 1177 m , 1147 s , 1105 m , 1025 s , 990 w , 956 w , 849 s , 823 m , 805 m , 766 s , 753 s , 561 s . $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.93 (*dt*, $^3J = 9$,

$^4J = 2.1$, $2H_n$ to MeO); 7.87 (*m*, $2H_m$ to $C\equiv C$, H–C(10)); 7.67 (*dt*, $^3J = 8.7$, $^4J = 1.8$, $2H_o$ to $C\equiv C$); 7.44 (*m*, H–C(3), H–C(5), H–C(7)); 7.21 (*m*, H–C(8), H–C(9)); 7.10 (*t*, $^3J = 9.3$, H–C(4)); 7.01 (*dt*, $^3J = 9$, $^4J = 2.1$, $2H_o$ to MeO); 3.88 (*s*, MeO); -0.195 (*d*, $^2J = 9$, H_a –C(11)); -0.38 (*dd*, $^2J = 9.3$, $^4J = 0.9$, H–C(11)). ^{13}C -NMR (75 MHz, $CDCl_3$): 162.3 (C_{ipso} to MeO); 151.9 (C_p to $C\equiv C$); 147.1 (C_p to MeO); 132.2, 131.4, 130.1, 129.0, 128.5, 127.5, 127.3, 126.4, 122.7 (arom. CH); 125.5 (C_{ipso} to $C\equiv C$); 122.1 (C(2)); 117.0, 115.8 (C(1), C(6)); 114.3 (C_o to MeO); 92.6, 89.9 ($C\equiv C$); 55.6 (MeO); 35.0 (C(11)). EI-MS (192°): 376 (54, M^+), 241 (34, $[M - N_2C_6H_4OMe]^+$), 135 (27, $N_2C_6H_4OMe^+$), 107 (100, $C_6N_4Me^+$). HR-MS: 376.1574 ($C_{26}H_{20}N_2O^+$; calc. 376.1576). Anal. calc. for $C_{26}H_{20}N_2O$: C 82.95, H 5.35, N 7.44; found: C 82.71, H 5.51, N 7.59.

{4-[(Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-2-yl)ethynyl]phenyl}(4-nitrophenyl)diazene (**11a**): From 4-bromo-4'-nitroazobenzene (**10a**; 230 mg, 0.75 mmol). CC (silica gel, hexane) gave 140 mg (48%) of **11a**. Dark red crystals. M.p. 167–168°. UV/VIS (CH_2Cl_2): 408 (4.39), 348 (4.37), 268 (4.60). IR (KBr): 3040w, 2922w, 2202w, 1699w, 1652s, 1591m, 1522s, 1447w, 1401w, 1344s, 1244m, 1141m, 1104m, 861m, 850m, 794m, 756s, 725w, 685m, 625m, 546w. 1H -NMR (300 MHz, $CDCl_3$): 8.39 (*dt*, $^3J = 9$, $^4J = 2.1$, $2H_o$ to NO_2); 8.19 (*dt*, $^3J = 9$, $^4J = 2.1$, $2H_n$ to $C\equiv C$); 7.98 (*dt*, $^3J = 8.4$, $^4J = 1.8$, $2H_a$ to NO_2); 7.87 (*d*, $^3J = 8.1$, H–C(10)); 7.72 (*dt*, $^3J = 8.4$, $^4J = 1.8$, $2H_o$ to $C\equiv C$); 7.48, 7.46 (*d*, 2H, *d*, 1H, $^3J = 9.6$, H–C(3), H–C(5), H–C(7)); 7.23 (*m*, H–C(8), H–C(9)); 7.13 (*t*, $^3J = 9.3$, H–C(4)); -0.19 (*d*, $^2J = 9.3$, H–C(11)); -0.35 (*d*, $^2J = 9.0$, H_b –C(11)). ^{13}C -NMR (75 MHz, $CDCl_3$): 155.5, 151.1 (C_p to $C\equiv C$, C_p to NO_2); 148.5 (C_{ipso} to NO_2); 127.7 (C_{ipso} to $C\equiv C$); 132.2, 131.4, 130.3, 128.7, 128.4, 127.7, 127.4, 127.2, 126.2, 124.6, 123.4, 123.3 (arom. CH); 121.4 (C(2)); 116.8, 115.6 (C(1), C(6)); 92.1, 91.3 ($C\equiv C$); 35.0 (C(11)). EI-MS (209°): (89, M^+), 239 (100, $[M - N_2C_6H_4NO_2]^+$). HR-MS: 391–1322 ($C_{25}H_{17}N_3O_2^+$; calc. 391.1322).

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