

1,1'-Biazulene derivatives. Syntheses and reactions

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Abstract

3,3'-Disubstituted 1,1'-biazulene derivatives were obtained in good yields starting from the dimers* of azulene-1-azo aromatic compounds and from the corresponding Schiff bases coupled at 3 positions.

Keywords: Biazulene synthesis, Schiff's bases

Introduction

Several different synthetic approaches to the compounds with the general formulae **1a-c** have been developed over the last fifty years.¹ However, the compounds attracted interest when it was found that some of them possess valuable non-linear optical properties.² Therefore, we have decided to develop more effective methods for the synthesis of these compounds and to study their structure and chemical properties. We have already reported the results for the compounds **1a** and **1b**.^{3,4}

Az-A=B-Ar	Az = substituted or unsubstituted 1-azulenyl
1a-c	Ar = substituted or unsubstituted aryl, heteroaryl or 1-azulenyl
a: A = B = N	
b: A = CH; B = N	
c: A = B = CH	

* The terms dimerization and dimer are used for coupling with the elimination of two hydrogen atoms and for the products resulted in these reactions, respectively.

One of the most interesting reactions of **1** consists in the single electron oxidation. It is well known that the low oxidation potential of the azulenes⁵ make them highly susceptible to oxidation which proceeds unselectively and in low yields.^{6,7} In contrast, Azulenes substituted with a double bond at C1 as in compound **1** display increased oxidation potential which allows for chemical^{3b,c,e} and electrochemical oxidation^{3d} without damage of the azulene skeleton. The dimers coupled at C1 were obtained as the main oxidation products. The almost complete conversion of the starting materials and the good yield of the dimers obtained inspired us to use this reaction for the syntheses of the interesting 1,1'-biazulenenes which until now have been obtained by Ullmann type coupling. As the starting coupling reagent, Morita and Takase⁸ have used ethyl 1-iodo-3-azulene carboxylate. In spite of the high coupling yield, the utility of the procedure for the syntheses of 1,1'-biazulene and their derivatives seems to be limited because of the difficult accessible starting materials and by the fact that the carboxylate group offers rather few possibilities for subsequent transformations.

In the present paper, two types of starting materials were considered for 1,1'-biazulene synthesis, namely bis azo derivatives **3** and bis Schiff bases, **5** (Scheme 1 and, Scheme 2, respectively). The compounds **3** and **5** were obtained by oxidation of the corresponding monomers **2**^{3b} and **4**^{3c} with anhydrous FeCl₃ in benzene. The influence of the substituent R on the oxidation in both cases was discussed^{3b,3c} and OCH₃ was found to be most favorable for dimer generation.

Results and Discussion

Reaction of azo-dimer

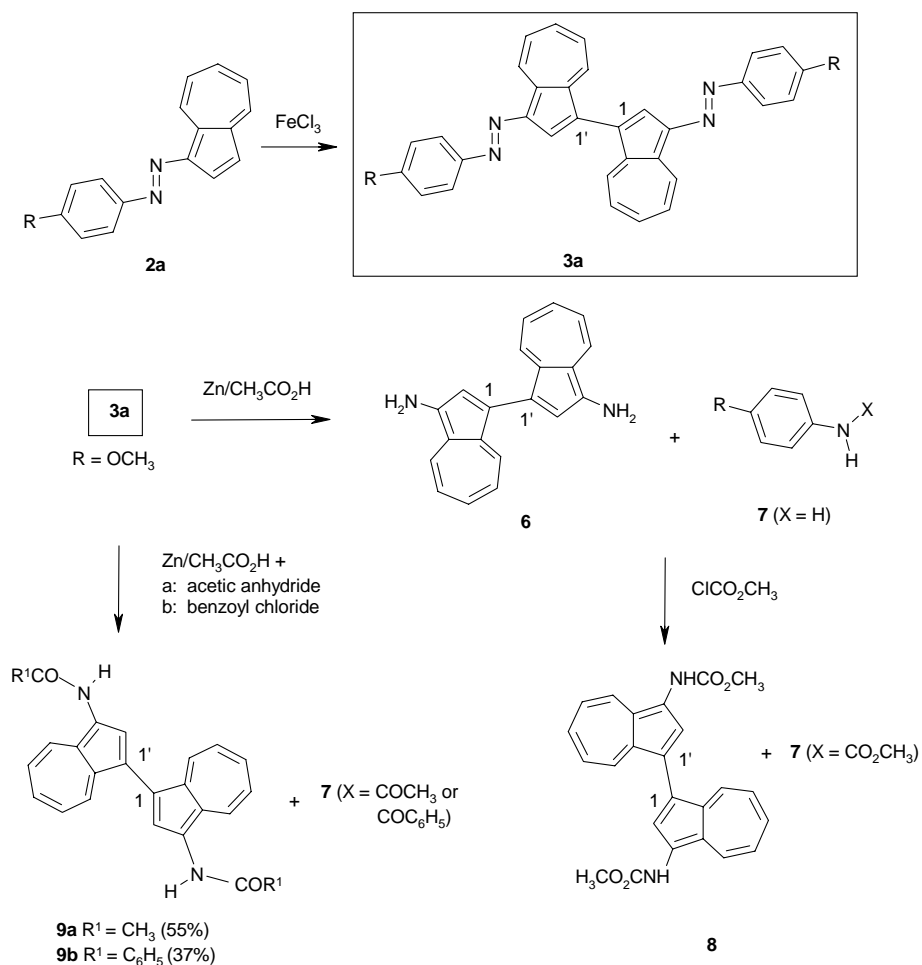
The reduction of 3,3'-bis-azo compound **3a** with zinc/acetic acid generated 3,3'-diamino-1,1'-biazulene, **6** and anisidine **7** (X = H). Unfortunately, the compound **6** was quite unstable and only ¹H- and ¹³C-NMR spectra could be recorded for this product in the mixture with **7** (X = H). However, the compound **6** could be quenched with methyl chloroformate to give the corresponding *bis*-methoxycarbamide **8** which was separated from the methoxycarbamide **7** (X = CO₂CH₃) and completely characterized.

When the reduction medium (Zn and acetic acid) acetic anhydride or benzoyl chloride was added, acylated *bis*-amines **9a** and **9b** were obtained together with acylated *para*-anisidine, **7** (X = CH₃CO or C₆H₅CO). The products were separated by column chromatography adding triethylamine to the eluent in order to avoid the destruction of the amides.

Our attempts to obtain *bis*-hydrazo compounds by reduction with hydrazine hydrate/Ni Raney failed and after treatment with methyl chloroformate only *bis*-methoxycarbamide **8** and **7** (X = CO₂CH₃) could be detected in low yields in the reaction mixture.

Reactions of Schiff base dimer

By the chemical oxidation (FeCl_3) of 1-azulene carbaldehyde only 3-chlorinated product was obtained (33 % yield) instead of the dialdehyde **11**. However, the generation of **11**, in 100 % yield, was realized by the hydrolysis of Schiff base dimers, **5** (Scheme 2). It is interesting that although the hydrolysis of Schiff base monomers, **4**, occurs fast, the corresponding dimers **5** react only slowly and in the presence of copper acetate as catalyst. A possible explanation for the observed difference is the low solubility of these dimers in the reaction medium. This convenient way

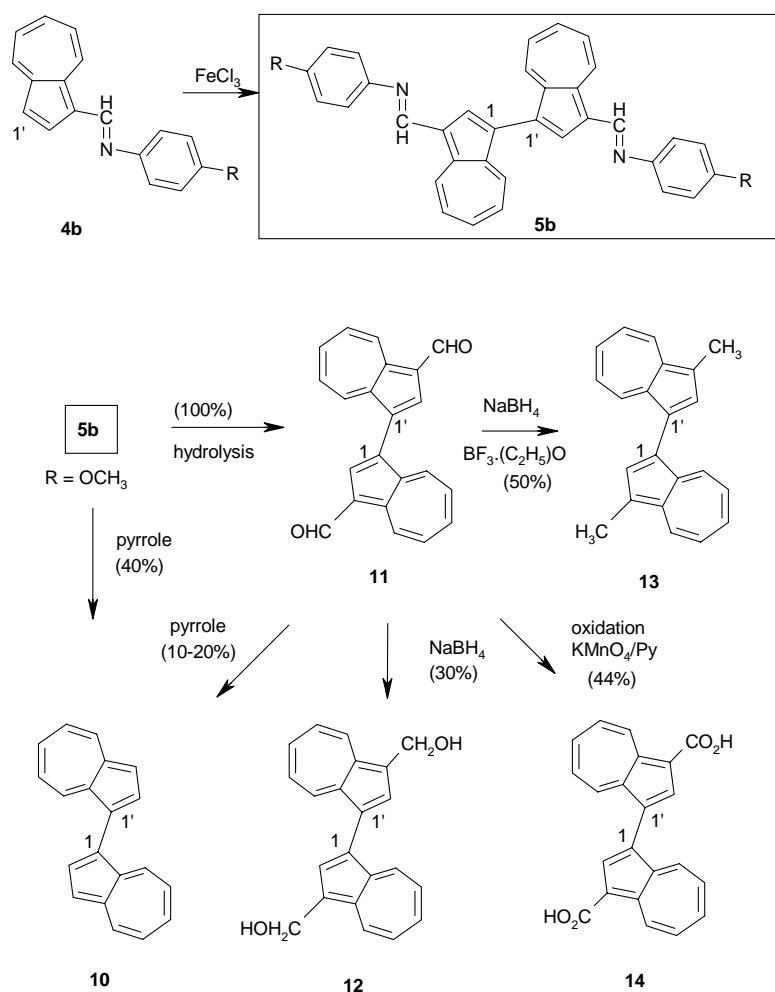


SCHEME 1

to access the dialdehyde **11** was important because the CHO group may be transformed to other functional groups. Thus, the diol **12** was generated by the reduction of **11** with NaBH_4 in methanol and the dicarboxylic acid **14** was formed by the oxidation with potassium permanganate in pyridine. Exhaustive reduction of **11** with NaBH_4 in the presence of $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ gave rise to 3,3'-dimethyl-1,1'-biazulene **13**. The reaction time for all these transformations was longer for the dimer than for the monomer, maybe due to the low solubility

of the dialdehyde **11**. The study of Wittig reaction of **11** is in progress. This reaction could represent the starting point for the syntheses of interesting large molecules containing azulene moieties and double bonds.

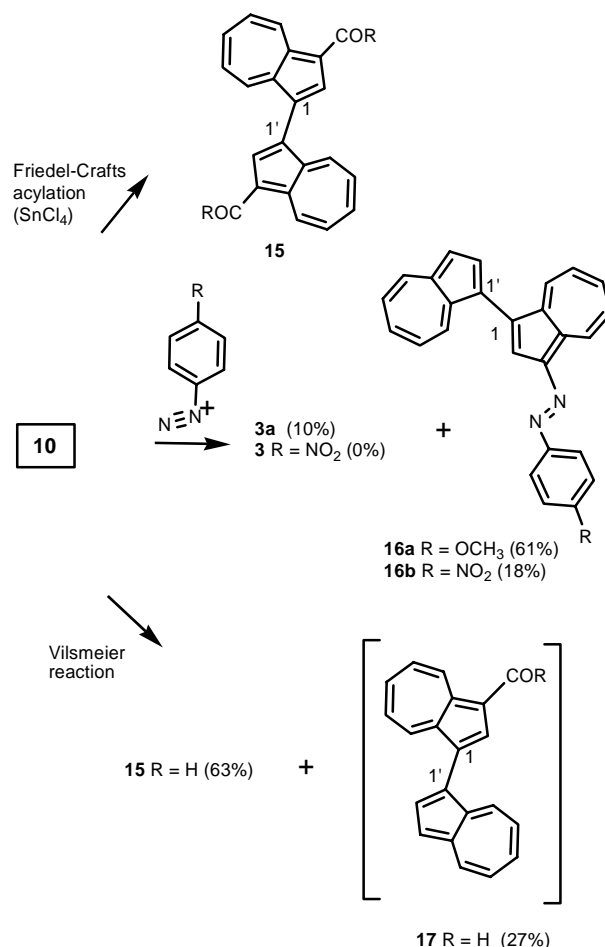
One of the useful reactions of the CHO group is its replacement with hydrogen. The reported yields⁹ for the decarbonylation of azulenic aldehydes in the presence of pyrrole under mild conditions were between 36 and 60%. By decarbonylation of dialdehyde **11** we obtained 1,1'-Biazulene **10** in only 10-20 % yields. However starting from the dimer Schiff base **5a** the yield was above 40 %. The reaction sequence: azulene \rightarrow 1-azulenecarbaldehyde \rightarrow corresponding Schiff base \rightarrow dimerization \rightarrow reaction with pyrrole that occurs in a very good over-all yield, represents an excellent way for the generation of hydrocarbon **10** starting from azulene.



The convenient access to **10** triggered a study of some reactions of this interesting hydrocarbon (Scheme 3). We have only studied reactions with electrophiles, which occur in

positions 3 and 3', some of which are reported below. Further investigations of reactions with nucleophiles or of redox and radical reactions are in progress.

Friedel Crafts acylation occurred in good yield in the presence of SnCl_4 as for the unsubstituted azulene.¹⁰ Reaction with acetyl chloride produced the diacetylated product **15** $\text{R} = \text{CH}_3$ in 58 % yield.



SCHEME 3

Vilsmeier acylation of **10** using the same protocol as for azulene¹¹ with equimolar amounts of dimethylformamide or dimethylacetamide gave the 3-substituted compound **17**. With excess of formylating agent the 3,3'-disubstituted compound **15** was formed. The coupling reaction with diazonium salts reported in a previous paper deals with the oxidation of azulene-1-azoaromatics.^{3b} Also in this reaction for $\text{R} = \text{OCH}_3$ **16a** and **3a** were generated, the major product being **16a**. It is noteworthy that the same reaction with the diazonium salt derived from 4-nitroaniline produced only monosubstituted product **16b** was formed.

In conclusion, we have showed that the relatively easy procedure for the dimerization of azocompounds **1a**^{3a,b} and their corresponding Schiff bases **1b**^{2d} represents a very good starting

point for the synthesis of many 1,1'-biazulene derivatives compounds otherwise difficult accessible.

Experimental Section

General Procedures. Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra: Beckman DK-2A, UV 5240. IR: Beckmann IR 5A. Mass spectra: Finnigan MAT 311-A/100MS. ^1H - and ^{13}C -NMR spectra: Bruker Avance DRX4 (^1H : 400 MHz, ^{13}C : 100 MHz) and Gemini 300 (^1H : 300 MHz, ^{13}C : 75 MHz), TMS was used as internal standard; when necessary, unequivocal signal assignment was confirmed by the analysis of the corresponding COSY and HETCOR spectra (the numbering for the exemplified compounds was indicated in Schemes and is not always correlated with the IUPAC nomenclature; when symmetrical products are described only one number in molecule is specified for both identical positions). Mass spectra: Finnigan MAT 311-A/100 MS and Carlo Erba QMD 1000. Column chromatography: basic alumina (activity BII-III (Brockmann)) or silica [70-230 mesh (ASTM)]. The dichloromethane (DCM) was distilled over calcium hydride.

Biazulene derivatives from the azo dimer **3a**

3,3'-Diamino-1,1'-biazulene (6). To a vigorously stirred solution of the dimer **3a** (52 mg, 0.1 mmol) in acetic acid (3 mL) at room temperature and under inert atmosphere, a large excess of powdered zinc (350 mg) was added in small portions in 15 min. The reduction was monitored by thin layer chromatography (TLC) and if necessary an additional amount of zinc was added. The mixture was stirred for 1 h when the color of the solution changed from brown to green. DCM (10 mL) was added to the suspension, the separated organic layer was carefully washed with 20 % aqueous sodium carbonate to neutralize the acetic acid, it was dried (Na_2SO_4) and filtered. The green DCM solution was used either for the amines separation or for the synthesis of *bis*-methoxycarbamide, **8**. After evaporation of the solvent in vacuum (with protection against air) gave the diamine **6** in a mixture with *para*-anisidine, **7** X = H. The amine **6** decomposes rapidly. NMR Data for **6**: ^1H -NMR (CDCl_3): δ 6.53 (t, $J = 9.6$ Hz, 2 H, H-5), 6.55 (t, $J = 9.6$ Hz, 2 H, H-7), 7.18 (t, $J = 9.6$ Hz, 2 H, H-6), 7.25 (s, 4 H, NH), 7.50 (s, 2 H, H-2), 7.75 (d, $J = 9.6$ Hz, 2 H, H-4), 7.90 (d, $J = 9.6$ Hz, 2 H, H-8); ^{13}C -NMR (CDCl_3): δ 117.7 (C-5), 120.1 (C-7), 123.2 (q), 123.5 (q), 125.8 (C-2), 131.8 (C-8), 133.7 (q), 134.6 (q), 136.0 (C-8), 138.8 (C-6).

3,3'-Bis(acetylamino)-1,1'-biazulene (9a). Dimer **3a** (52 mg, 0.1 mmol) and potassium acetate (0.1 g) were dissolved in a mixture of acetic anhydride (3 mL) and acetic acid (3 mL). To the strongly stirred solution at room temperature and under inert atmosphere a large excess of powdered zinc (350 mg) was added in small portions during 15 min; the reduction was monitored by TLC (when necessary a supplementary amount of zinc must be added). The mixture was stirred for one additional hour when the color of the solution changed from brown to green. To the reaction mixture DCM (25 mL) was added and the obtained solution was washed

with water (25 mL), aqueous ammonia (10 %, 2 x 25 mL) and water (25 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent was vaporized. The residue was chromatographed on alumina, eluent DCM:triethylamine, 9:1 and the first colored fraction was collected. After solvent vaporization, the residue was washed several times with ethyl ether in small portions. The amount of the product **8a** was 20 mg (55 % yield). Green crystals, m. p. 247 °C, (ether), IR (KBr): ν_{max} 765 (m), 1135 (m), 1330 (m), 1370 (m), 1400 (sh), 1440 (m), 1520 (m), 1560 (s), 1590 (m), 1645 (s), 2390 (m), 3045 (m), 3200-3300 cm^{-1} ; UV (MeOH): λ_{max} [nm] (log ϵ): 210 (4.26), 227 (4.41), 250 (4.46), 278 (4.54), 298 sh (4.49), 309 sh (4.44), 316 sh (4.40), 398 (4.06), 610 (2.66), 668 (2.68); ^1H NMR (DMSO- d_6): δ 2.23 (s, 6 H, CH_3), 6.97 (t, $J = 9.6$ Hz, 2 H, H-5), 7.02 (t, $J = 9.6$ Hz, 2 H, H-7), 7.56 (t, $J = 9.6$ Hz, 2 H, H-6), 8.14 (d, $J = 9.6$ Hz, 2 H, H-4), 8.30 (d, $J = 9.6$, 2 H, H-8), 8.47 (s, 2 H, H-2), 10.27 (s, 2 H, NH); ^{13}C NMR (DMSO- d_6) δ : 23.48 (CH_3), 120.9 (C-5), 122.3 (C-7), 122.8 (q), 126.2 (q), 127.7 (q), 130.5 (C-2), 132.5 (q), 133.6 (C-4), 136.2 (C-8), 139.8 (C-6), 168.1 (CO); MS (EI): 369 ($\text{M}^+ + 1$, 22%), 368 (M^+ , 100), 348 ($\text{M}^+ - \text{H}_2\text{O} - 2\text{H}$, 10), 326 ($\text{M}^+ - \text{Ac} + \text{H}$, 19), 325 ($\text{M}^+ - \text{Ac}$, 38), 305 ($\text{M}^+ - \text{Ac} - \text{H}_2\text{O} - 2\text{H}$, 8), 283 ($\text{M}^+ - 2\text{Ac}$, 12), 282 ($\text{M}^+ - 2\text{Ac} - \text{H}$, 11), 281 ($\text{M}^+ - 2\text{Ac} - 2\text{H}$, 10), 268 (8), 267 (14), 266 (13), 254 (14); Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ (%): C 78.23, H 5.47, N 7.60; found C 77.96 %, H 5.73, N 7.71.

3,3'-Bis(benzoylamino)-1,1'-biazulene (9b). To the strongly stirred solution of the dimer **3a** (52 mg, 0.1 mmol) in acetic acid (3 mL) at room temperature under inert atmosphere, a large excess of powdered zinc (350 mg) was added in small portions during 1 hour. The reduction was monitored by thin layer chromatography and when necessary, a supplementary amount of zinc had to be added. The color of the solution changed from brown to green. After dilution with DCM (5 mL) the solution was cooled at 0 °C and 20 % aqueous sodium carbonate (1 mL) and benzoyl chloride in excess (1 mL) were added. The solution was stirred at 0 °C for 90 min. After the dilution with DCM (20 mL) the mixture was washed with water, aqueous ammonia (20 %) and again with water. It is important to eliminate the excess of benzoyl chloride otherwise it hydrolyzes on the column chromatography with the HCl generation and completely destroy the product. The organic layer was dried (Na_2SO_4) and the solvent vaporized in vacuum. The chromatography on alumina eluent DCM:triethylamine 9:1 afforded product **8b** as the first colored fraction (18 mg, 37 % yield). Green crystals, m. p. 175 °C, ether, IR (KBr): ν_{max} 710 (s), 740 (m), 800 (m), 870 (m), 1033 (m), 1080 (m), 1130 (m), 1275 (m), 1368 (m), 1400 (m), 1518 (m), 1543 (m), 1570 (m), 1645 (s), 2970 (m), 3260 (s) cm^{-1} ; UV (MeOH): λ_{max} [nm] (log ϵ): 212 (4.47), 228 (4.54), 236 sh (4.53), 242 sh (4.53), 278 (4.53), 289 sh (4.52), 306 sh (4.52), 373 (4.03); ^1H NMR (DMSO- d_6): δ 7.09 (t, $J = 10.4$ Hz, 2 H, H-5), 7.11 (t, $J = 9.6$ Hz, 2 H, H-7), 7.58 (t, $J = 6.4$ Hz, 4 H, H-3'', H-5''), 7.60 (t, $J = 6.4$ Hz, 2 H, H-4''), 7.64 (t, $J = 9.8$ Hz, 2 H, H-6), 8.11 (d, $J = 6.6$ Hz, 4 H, H-2'', H-6''), 8.30 (d, $J = 9.6$ Hz, 2 H, H-4), 8.46 (s, 2 H, H-2), 8.53 (d, $J = 10.0$ Hz, 2 H, H-8), 10.62 (s, 2 H, NH); ^{13}C NMR (DMSO- d_6): δ 121.9 (C-7), 122.8 (q), 123.1 (C-5), 125.6 (q), 127.8 (C-4''), 128.1 (C-3'', C-5''), 128.6 (C-2'', C-6''), 129.8 (q), 132.6 (C-2), 132.6 (C-8), 133.7 (q), 136.5 (C-4), 140.1 (C-6), 134.9 (q); MS (EI): 493 ($\text{M}^+ + 1$, 16%), 492 (M^+ , 61), 472 ($\text{M}^+ - \text{H}_2\text{O} - 2\text{H}$, 18), 388 ($\text{M}^+ - \text{Bz} + \text{H}$, 21), 387 ($\text{M}^+ - \text{Bz}$, 26), 367 ($\text{M}^+ - \text{Bz} - \text{H}_2\text{O} - 2\text{H}$, 18), 281 ($\text{M}^+ - 2\text{Bz} - \text{H}$, 11), 266 (7), 265 (3), 264 (4), 254 (8), 253 (5), 252 (2), 247 (6),

105 (Bz, 100), 77 (Ph, 69); Calculated for $C_{34}H_{24}N_2O_2$ (%): C 82.93, H 4.88, N 5.69; found C 82.88 %, H 4.95, N 5.65.

3,3'-Bis(methoxycarbamide)-1,1'-biazulene (8). To the solution of the *bis*-amine **6**, and anisidine, **7** = H, cooled at 0 °C, 20 % aqueous sodium carbonate (1 mL) was added followed by an excess of methyl chloroformate (0.5 mL). The reaction mixture was stirred for 90 min at 0 °C and the work-up was the same as for compound **9b**. The product collected as the first fraction represents probably a ureide because in the NMR spectrum methoxy group failed. The second green fraction represents the product **8** (12 mg, 30 % yield), green crystals, m. p. 198 °C ether, IR (KBr): ν_{\max} 740 (m), 1130 (m), 1220 (m), 1230 (m), 1375 (m), 1390 (m), 1570 (m), 1655 (s), 2920 (m), 3200-3300 cm^{-1} ; UV (MeOH): λ_{\max} [nm] (log ϵ): 226 (4.36), 250 (4.41), 281 (4.60), 298 sh (4.52), 373 (4.03); 1H NMR (DMSO- d_6): δ 4.46 (s, 6 H, CH_3), 7.04 (t, J = 10.0 Hz, 2 H, H-5), 7.12 (t, J = 9.6 Hz, 2 H, H-7), 7.62 (t, J = 9.6 Hz, 2 H, H-6), 8.20 (d, J = 10.0 Hz, 2 H, H-4), 8.47 (s, 2 H, H-2), 8.49 (d, J = 9.6 Hz, 2 H, H-8), 10.67 (s, 2 H, NH); ^{13}C -RMN (DMSO- d_6): 43.15 (OCH_3), 121.4 (C-7), 122.7 (C-1,C-5), 124.8 (C-3), 128.0 (q), 130.3 (C-2), 132.7 (q), 133.4 (C-8), 136.3 (C-4), 139.9 (C-6), 164.4 (CO); Calculated for $C_{24}H_{20}N_2O_4$ (%): C 72.00, H 5.00, N 7.00; found C 72.16 %, H 5.13, N 7.01.

Biazulene derivatives from the Schiff base dimer **5a**

1,1'-Biazulene-3,3'-dicarbaldehyde (11). To the solution of **5a** (150 mg, 0.288 mmol) in ethanol/water, 2/1 vol (mL), copper acetate (100 mg) was added and the mixture was vigorously refluxed for 24 hours. Water (50 mL) was added, the solution was acidified with 10 % HCl solution and the ethanol was vaporized in vacuum. The aqueous solution was extracted twice with DCM. The extract was washed with water, saturated $NaHCO_3$ solution and again with water and some drops of triethylamine were added. After drying, the solution was filtered on thin alumina layer, DCM was vaporized in vacuum and the dialdehyde **11** was obtained as brown microcrystalline powder (175 mg, yield 100%), mp 254-255 °C (lit.^{3e} 254-256 °C).

1,1'-Biazulene (10). A. From the dimer 5a. A solution of **5a** (300 mg, 0.576 mmol) and pyrrole (750 mg, 11.4 mmol) in acetic acid (9 mL) was stirred at room temperature under inert atmosphere for 7 days. The solvent was rotary-evaporated, and the residue was diluted with DCM. The organic solution was washed with 5 % aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The chromatography of the residue on alumina with benzene afforded the product **10**, (59 mg, yield 43 %). Using ethyl acetate as eluent, the second fraction can be obtained, representing a mixture of Schiff base **5a** and aldehyde **11** in ratio 1.5/1 (14 mg mixture, conversion of **5a** 95 %). The dimer **10** has the same characteristics as the product reported by Morita.⁹

B. From the bis-1,1'-azulene-3,3'-dicarbaldehyde (11). The dialdehyde **11** (100 mg, 0.322 mmol) and pyrrol (417 mg, 6.3 mmol) were dissolved in acetic acid (2 mL) and DCM (2 mL).⁹ After 3 days the starting material was completely transformed. After work-up, the residue was separated by chromatography on alumina. The benzene eluted the dimer **10** (5 mg,

yield 13 %), and DCM eluted 1,1'-biazulene-3-carbaldehyde, **17** R = H (5 mg, yield 11 %), which is characterized below.

3,3'-Dihydroxymethyl-1,1'-biazulene (12). The dialdehyde **11** (62 mg, 0.2 mmols) was reduced with an excess of NaBH₄ in methanol 1 h. After the usual work-up, the mixture was separated by chromatography on alumina and three fractions were collected: *fraction 1* (16 mg), eluted with ethyl acetate : n-pentane = 1:2 contains mainly the starting material and unidentified minor compounds (from the ¹H-NMR spectrum), *fraction 2* (4 mg) eluted with ethyl acetate contains unidentified compounds and *fraction 3* (18 mg) eluted with methanol represents the diol **12** (yield 30 %). The diol decomposes in time, however, its characterization was accomplished. The compound **12**, green-black solid (dec. 210 °C), IR (DCM): ν_{\max} 3400-3650 cm⁻¹ (OH); ¹H-NMR (CDCl₃): δ 1.72 (bs, 2 H, 3 CH₂-OH), 5.26 (s, 4 H, 3 CH₂-OH), 7.08 (t, *J* = 10 Hz, 2 H, H-5), 7.20 (t, *J* = 10 Hz, 2 H, H-7), 7.61 (t, *J* = 10 Hz, 2 H, H-6), 8.10 (s, 2 H, H-2), 8.35 (d, *J* = 10 Hz, 2 H, H-8), 8.53 (d, *J* = 10 Hz, 2 H, H-4); ¹³C-NMR (CDCl₃): δ 58.6 (3-CH₂), 123.0 (C-5), 123.4 (C-7), 124.9 (q), 128.6 (q), 129.0 (q), 134.2 (C-8), 136.6 (C-4), 137.7 (q), 138.7 (C-6), 138.8 (C-2); MS (EI): 316 (M⁺+2, 24%), 296 (M⁺-H₂O, 44), 282 (M⁺-H-CH₂OH, 90), 265 (M⁺-CH₂OH-H₂O, 56), 252 (M⁺-2CH₂OH, 100), 126 ((M-2CH₂OH)²⁺, 40).

3,3'-Dimethyl-1,1'-biazulene (13). Dialdehyde **11** (45 mg, 0.16 mmols) was reduced with an excess of NaBH₄ and BF₃·Et₂O in diethyl ether-diglyme¹² and the hydrocarbon **13** (20 mg, yield 50 %) was obtained as dark green crystals, mp 92–94 °C.^{6c} The ¹H-NMR and MS spectra were identical with those described by Nozoe and colab.^{6c} UV (hexane): λ_{\max} [nm] (log ϵ) 226 (4.22), 250 sh (4.31), 269 (4.58), 303 (4.31), 315 (4.37), 401 (3.971); ¹³C-NMR (CDCl₃): δ 12.7 (3-CH₃), 121.1 (C-7), 121.9 (C-5), 124.9 (q), 125.6 (q), 133.8 (C-4), 135.8 (C-8), 136.6 (q), 137.6 (q), 138.1 (C-6), 139.4 (C-2).

1,1'-Biazulene-3,3'-dicarboxylic acid (14). Dialdehyde **11** (31 mg, 0.1 mmols) was oxidized¹³ with KMnO₄ (31 mg, 0.19 mmols) in pyridine (2.5 mL) and after common work-up, 1,1'-biazulene-3,3'-dicarboxylic acid, **14**, (15 mg, 44 %) were obtained, green-brown crystals, mp 290–292 °C (Lit.^{6c} 290-293 °C). ¹H-NMR and MS spectra were identical with that reported.^{6c}

Biazulene derivatives from the 1,1'-biazulene (10).

Vilsmeier reaction. The Vilsmeier complex obtained from phosphoryl chloride (82 mg, 0.53 mmol) and DMF (0.25 mL) at 0 °C under inert atmosphere was added slowly to a solution of **10** (50 mg, 0.23 mmol) in DMF (0.4 mL) under stirring. After 30 min the mixture was quenched in ice and 2M aqueous NaOH was added until pH alkaline. After the extraction with DCM, the organic layer was washed with water, dried (Na₂SO₄) and concentrated in vacuum. The residue was chromatographed on alumina with DCM and two fractions were collected: *fraction 1*, starting material, (4 mg, conversion 92 %) and *fraction 2*, 1,1'-biazulene-3-carbaldehyde, **17** R = H, (32 mg, 0.113 mmol, yield 63 %). With ethyl acetate eluted dialdehyde, **11** (15 mg, yield 27 %).

When an excess of Vilsmeier complex [from phosphoryl chloride (164 mg, 1.06 mmol) and DMF (0.5 mL)] was added to the solution of **10** (50 mg, 0.23 mmol) in DMF (0.4 mL), after 30 min, only dialdehyde **11** resulted (conversion 100 % and yield 70 %).

1,1'-Biazulene-3-carbaldehyde, 17 R = H, green-brown crystals, mp 65-67 °C, IR (DCM): ν_{\max} 1140, 1450, 1585, 1655, 3060 cm^{-1} ; UV (dioxane): λ_{\max} [nm] (log ϵ): 240 (4.46), 267 (4.50), 296 (4.63), 321 (4.63), 588 (2.83); ^1H NMR (CDCl_3): δ 7.11 (t, $J = 10$ Hz, 1 H, H-5'), 7.22 (t, $J = 10$ Hz, 1 H, H-7'), 7.44 (t, $J = 10$ Hz, 1 H, H-7), 7.56 (d, $J = 4$ Hz, 1 H, H-3'), 7.63 (t, $J = 10$ Hz, 1 H, H-6'), 7.63 (t, $J = 10$ Hz, 1 H, H-5), 7.86 (t, $J = 10$ Hz, 1 H, H-6), 8.09 (d, $J = 4$ Hz, 1 H, H-2'), 8.32 (d, $J = 9.8$ Hz, 1 H, H-4'), 8.43 (d, $J = 9.8$ Hz, 1 H, H-8'), 8.47 (s, 1 H, H-2), 8.54 (d, $J = 10$ Hz, 1 H, H-8), 9.64 (d, $J = 10$ Hz, 1 H, H-4), 10.49 (s, 1 H, CHO); ^{13}C NMR (CDCl_3): δ 117.6 (C-3'), 123.3 (C-5'), 123.4 (C-7'), 124.7 (q), 125.1 (q), 127.8 (q), 128.2 (C-7), 129.4 (C-6'), 135.8 (C-4'), 137.0 (q), 137.3 (C-8'), 137.6 (C-4), 138.3 (C-2'), 138.4 (C-5), 138.5 (C-8), 140.4 (C-6), 141.2 (q), 141.5 (q), 142.9 (C-2), 143.2 (q), 186.6 (CHO); MS (EI): 284 ($\text{M}^+ + 2$, 2%), 283 ($\text{M}^+ + 1$, 22), 282 (M^+ , 100), 281 ($\text{M}^+ - 1$, 7), 253 (25), 252 (70), 250 (26), 126 (49), 125 (26).

Friedel-Crafts acylation. A mixture of **10** (58 mg, 0.112 mmol), SnCl_4 (0.4 mL) and acetyl chloride in large excess (20 mL) was refluxed for 20 min in tetrachloromethane (35 mL). The reaction mixture was quenched in water (600 mL) and extracted with diethyl ether. The extract was washed with water, dried (Na_2SO_4) and the solvent was vaporized in vacuum. The crude material was chromatographed on alumina (eluent, n-pentane:DCM, 1:1) and 3,3'-diacetyl-1,1'-biazulene, **15** R = CH_3 was collected as the colored fraction (22 mg, yield 58 %).

3,3'-Diacetyl-1,1'-biazulene (15). R = CH_3 , green crystals, mp 248-250 °C, IR (DCM): ν_{\max} 1160, 1190, 1220, 1360, 1450, 1640, 2995, 3070 cm^{-1} ; UV (dioxane): λ_{\max} [nm] (log ϵ): 239 (4.52), 290 (4.75), 309 (4.68), 392 (4.13), 581 (2.81); ^1H NMR (CDCl_3): δ 2.78 (s, 6 H, CH_3), 7.41 (t, $J = 9.8$ Hz, 2 H, H-7), 7.66 (t, $J = 9.8$ Hz, 2 H, H-5), 7.86 (t, $J = 9.8$ Hz, 2 H, H-6), 8.36 (d, $J = 9.8$ Hz, 2 H, H-8), 8.44 (s, 2 H, H-2), 9.98 (d, $J = 9.8$ Hz, 2 H, H-4); ^{13}C NMR (CDCl_3): δ 29.3 (CH_3), 124.2 (q), 124.7 (q), 127.5 (C-7), 129.6 (C-5), 137.6 (C-4), 140.0 (C-8), 140.3 (C-6), 140.7 (q), 141.8 (C-2), 142.3 (q), 195.5 (CHO); MS (EI): 340 ($\text{M}^+ + 2$, 4%), 339 ($\text{M}^+ + 1$, 23), 338 (M^+ , 100), 323 ($\text{M}^+ - \text{CH}_3$, 58), 252 ($\text{M}^+ - 2\text{COCH}_3$, 62), 250 (37), 154 (50), 125 (35).

Coupling reaction with diazonium salts. A solution of 4-nitrophenyldiazonium chloride, prepared at 0 °C from 4-nitroaniline (100 mg, 0.72 mmol), 37 % aqueous HCl (3 mL) and sodium nitrite (50 mg, 0.72 mmol) in water (2 mL), was added slowly to a stirred solution of 1,1'-biazulene (75 mg, 0.29 mmol) and sodium acetate (230 mg) in ethanol (20 mL). After stirring at 0 °C for 30 min and then at room temperature for 3h and work-up, the crude material was separated on silica with benzene resulting *fraction 1*, unreacted biazulene (5 mg, conversion 93 %); *fraction 2*, the product 3-(4''-nitrophenylazo)-1,1'-biazulene, **16b** (20 mg, yield 18%) (the disubstituted product failed).

3-(4-Nitrophenylazo)-1,1'-biazulene (16b). brown needles, mp 170-171 °C IR (DCM): ν_{\max} 1110, 1150, 1190, 1340, 1520, 1580 cm^{-1} ; UV (dioxane): λ_{\max} [nm] (log ϵ): 242 (4.50), 272 (4.49), 294 (4.48), 306 (4.47), 403 (4.35), 513 (4.18); ^1H NMR (CDCl_3): δ 7.17 (t, $J = 10$ Hz, 1 H, H-5'), 7.24 (t, $J = 10$ Hz, 1 H, H-7'), 7.37 (t, $J = 10$ Hz, 1 H, H-7), 7.56 (d, $J = 4$ Hz, 1 H, H-3'), 7.58 (t, $J = 10$ Hz, 1 H, H-5), 7.65 (t, $J = 10$ Hz, 1 H, H-6'), 7.83 (t, $J = 9.6$ Hz, 1 H, H-6),

8.08 (dd, $J = 8.8$, 2 Hz, 2 H, H-3'', H-5''), 8.12 (d, $J = 4$ Hz, 1 H, H-2'), 8.37 (dd, $J = 9.2$, 2 Hz, 2 H, H-2'', H-6''), 8.42-8.48 (m, 4 H, H-2, H-4', H-8, H-8'), 9.43 (d, $J = 3.6$ Hz, 1 H, H-4); MS (EI): 404 ($M^+ + 1$, 17%), 403 (M^+ , 66), 402 ($M^+ - 1$, 55), 373 (24), 372 (23), 269 (29), 253 (40), 252 (100), 250 (45).

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