Syntheses of polycyclic compounds by oxidative coupling of azulene-1-azoarenes

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The chemical oxidation of azulene-1-azoarenes with $FeCl_3$ in benzene was studied. For unsubstituted azo compounds, a 4′,4′ coupling takes place yielding biarylic derivatives **4** or **6**. 4′-Substituted azulene-1-azobenzenes react depending on the nature of the substituent. Electron-withdrawing substituents such as NO_2 increase the oxidation potential of the starting azo compounds and, as a consequence, they hinder the oxidative coupling. On the contrary, electron-releasing substituents such as 4′-methoxy (compound **1b**) activate the position 3 in the azulene moiety and coupling in this position takes place as the main pathway; products with three and four azulene moieties coupled in the 1 and 3 positions (**11** and **12**) were also separated and characterized. The coupling product for the oxidation of compound **1c** with a 4′-CH_3 substituent results in 15% yield only; large amounts of oligomers and polymers with substituted methyl detected in the reaction mixture prove that in **1c** the benzylic position is also a reactive one. A mechanism with a radical cation intermediate generated by the single-electron transfer oxidation of the starting azo compounds is proposed.

The dimerization† of aromatic radical cations is well known as one of the most important reactions of these intermediates and often the presence of a dimer in the oxidation of an aromatic compound is strong evidence for single-electron transfer intervention with the generation of a radical cation.[1] Coupling reactions have been observed in anodic[2] or chemical oxidations using various oxidizing agents such as metal salts (*e.g.* $FeCl_3$,[3] $CuCl_2$,[4] $Tl(F_3CCO_2)_3$[5] or $MeBu_3N^+MnO_4$[6]) or reagents such as NO^+.[1b] Many aromatic carbocyclic[1-6] or heterocyclic compounds[7] have been investigated in such oxidations, to study the reaction conditions and mechanism and to synthesize interesting compounds (*e.g.* BINOL (1,1′-binaphthol) or NOBIN (±)-2-amino-2′-hydroxy-1,1′-binaphthyl) compounds with a 1,1′-binaphthyl skeleton).

For azulene compounds, however, few single-electron transfer oxidations have been reported.[8] The electrochemical oxidation[9] of azulene leads to regioselective 1,3-coupling; oligo- and polyazulenes were obtained because the dimer formed as intermediate in the reaction has a lower oxidation potential than the monomer.[10] If both 1 and 3 positions are occupied, the dimerization becomes reversible. A 3,3′-disubstituted 1,1′-dimer, however, is obtained from 1-substituted azulenes.[9] The limited range of oxidation agents for azulene coupling as compared to the oxidation of other aromatic compounds can be explained if one compares the oxidation potentials of azulenic[10] and benzenoid aromatics[11] (see Table 1). The low oxidation potential for azulenes can promote advanced oxidation with the destruction of the skeleton.

However, some successful oxidative dimerizations of azulenic compounds have been reported. Thus, in the oxidation of naphtho[2,3-*a*]azulenehydroquinone with $FeCl_3$,[12] the corresponding dimer was formed as the main product, while during the oxidation of 4,6,8-trimethylazulene with $ArPb(AcO)_3$ in trifluoroacetic acid the dimer results as a by-product (in 4% yield) and a 1-aryl substituted product is formed in 27% yield.[13] In the

Table 1 Oxidation potentials (E/V *vs.* SCE) of some azulenes and benzenoid aromatic hydrocarbons

Compound	E/V *vs.* SCE
Azulene	0.88
2,4,6-Trimethylazulene	0.83
Guajazulene[a]	0.65
Benzene	2.34
Naphthalene	1.14
Perylene	0.85

[a] The IUPAC name for guajazulene is 1,4-dimethyl-7-isopropylazulene.

autoxidation of some azulenic hydrocarbons in aprotic solvents, among a wide variety of products, dimers were separated in low yields (5%).[14] Azulene and its alkyl derivatives were oxidized also in a UV-irradiated stationary system by $(F_3CCO_2)_2Hg$.[15] All these dimerizations were rationalized in terms of radical-cation coupling. EPR and ENDOR studies[8,15] and quantum chemical calculations[16] for radical cations obtained from azulenic hydrocarbons support their tendency towards a 1,1′-coupling mechanism.

During our studies on the halogenation of azulene-1-azoarenes with cupric chloride[17] we have observed that for 4′-substituted derivatives, the 3,3′-dimer is, sometimes, obtained (<5% yield) along with the 3-halogenated product. This fact suggests the possible generation of a radical cation as an intermediate in the reaction.

The peculiarity of azulene-1-azoarenes consists in the simultaneous presence of both alternant and nonalternant aromatic moieties. Our preliminary studies on the electronic structure of the azulene-1-azoarenes[18] confirm the highest charge density in position 3 (and 1) in the neutral molecule in accordance with the regioselectivity of halogenation in this position. However, the spin distribution in the corresponding radical cations is more randomized; position 4′ is most favoured, followed by position 3. The presence of the azo group increases the oxidation potential of the azulene moiety and protects it against destructive oxidation. The increase of oxidation power from

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† The terms dimerization and dimer (or trimer) are used for coupling with the elimination of two hydrogen atoms and for the products resulting from these reactions, respectively.

CuCl$_2$ to FeCl$_3$ together with the decrease of halogenation aptitude suggested that we use FeCl$_3$ for generating radical cations from azulene derivatives. In the present paper we describe the results of our studies on the formation and behaviour of azulene-1-azoarene radical cations.

Results and discussion

We investigated the oxidation of unsubstituted azulene-1-azoarenes (**1a** and **2**), 4′-phenyl-substituted derivatives (**1b**–**1d**)

1a R = H
1b R = OCH$_3$
1c R = CH$_3$
**1d** R = NO$_2$

2

3
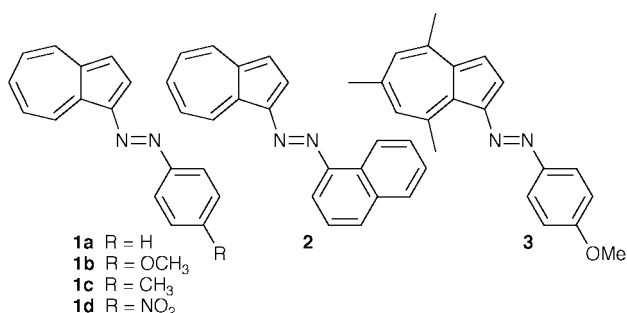
and 4,6,8-trimethylazulene-1-azo-(4′-methoxybenzene), **3**, with a hindered 3-position. The synthesis of the azo compounds followed the procedures described by Gerson *et al.*,[19] Anderson *et al.*[20] and by us.[17]

The oxidation was performed using an excess of ferric chloride (FeCl$_3$–azo compound 4:1), in benzene, at room temperature, without protection from the air. After work-up, the products were separated by column chromatography and, when necessary, were purified by crystallization.

Oxidation of azulene-1-azobenzene (1a) and azulene-1-azo-1′-naphthalene (2)

The oxidation of **1a** gave the products presented in Scheme 1


4 (38%)

5 (17%)
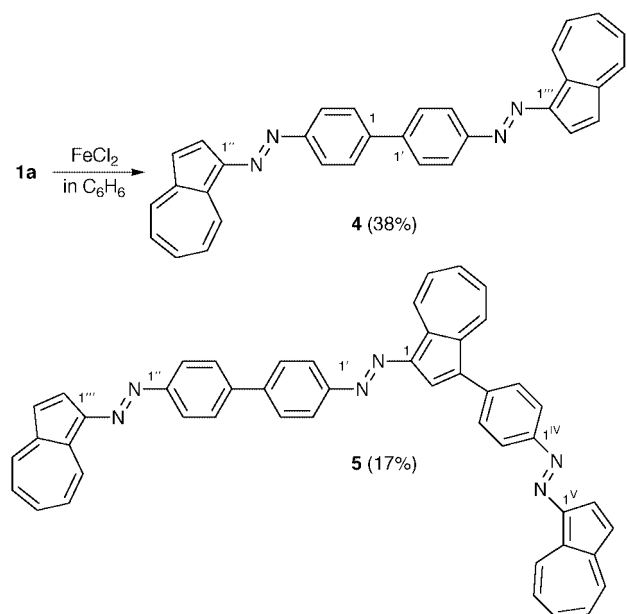
Scheme 1

(the starting material conversion was 91%). After the elution of unreacted **1a**, the second fraction contains the main product, **4**, with a dimeric structure as suggested from its mass spectrum (*m/z* = 462). There are no significant differences between the azulene proton signals in the ^{1}H-NMR spectra of **4** and **1a** proving that the azulene ring remains almost unchanged. In contrast, the complex phenyl signals for **1a** are replaced in the

product **4** by an AB spin system for eight protons (δ 7.85 and 8.10 ppm, *J* 8.6 Hz), typical for a *para*-substituted benzene, supplying the proof for *para* coupling of **1a**. The ^{13}C-NMR spectrum is in agreement with the suggested structure. The presence of the biphenyl skeleton in **4** was proved also by the synthesis of this compound *via* coupling of the benzidine bis-diazonium salt with azulene in excess (yield, 78%).

For the third isolated compound (**5**), a trimeric structure was suggested by the mass spectrum results (*m/z* = 692). The presence in the ^{1}H-NMR spectrum of three AB signal groups (δ 7.86, 7.93, 7.94 and 8.09, 8.13, 8.16 ppm, respectively, *J* 8.5 Hz), each for four protons, indicates the presence of three phenyl groups substituted in the *para* positions. That means that two phenyl groups are coupled together as in the dimer **4** whereas the third must be *para*-coupled with an azulene moiety. This supposition was confirmed by the presence of a singlet for one proton at δ 8.52 ppm, typical for position 2 in 3-substituted azulene-1-azo-derivatives (2-H). Also, the two doublets at δ 8.33 and 8.35 ppm (*J* 4.6 Hz), each for one proton (2‴-H and 2^V-H), are in accord with the presence in the product **5** of two unsubstituted and different 1-azoazulene groups; the proposed structure was confirmed also by other proton signals. The last eluted fractions were mixtures of oligomers (from ^{1}H-NMR signals); a small amount of polymers remained on the column.

Similarly as for **1a**, the oxidative dimerization of azulene-1-azo-1′-naphthalene (**2**) occurs especially at the 4′-naphthyl position. The compounds reported in Scheme 2 were separated

6 (87.5%)

7 (7.5%)
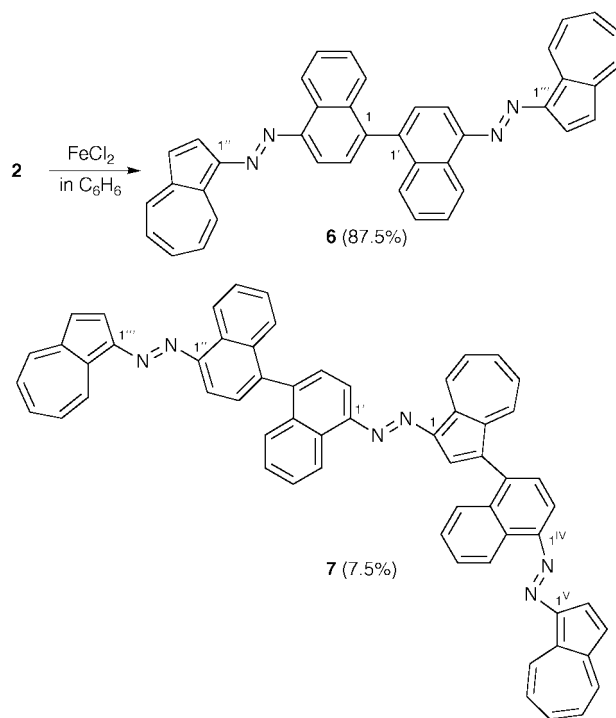
Scheme 2

by chromatography from the reaction mixture (the conversion of **2** was 77%).

After the elution of the starting material, the second fraction contains the main product, **6**, with a dimer structure (*m/z* = 562). The chemical shifts of azulene signals in ^{1}H-NMR for **2** and **6** are not dramatically different. Compound **6** presents an AB spin system for four naphthyl protons (δ 7.68 and 8.18 ppm, *J* 7.6 Hz) indicating that the coupling of the two molecules of **2** takes place at position 4′ of the naphthalene moiety (the other signals in NMR spectra are in accord with the proposed structure for **6**) whereas the azulene moiety remains unchanged.

From the mass spectrum of the second separated product **7** ($m/z = 842$) and the comparison with the structure of compound **5**, resulting from the oxidation of **1a**, a trimeric structure was assigned for **7**. Indeed, in the range characteristic for the proton in position 2 of the 1-azoazulenyl group, the ^{1}H-NMR spectrum presents a singlet (δ 8.76 ppm) and two doublets (δ 8.55 and 8.57 ppm, J 4.4 Hz), each for one proton. This attests the presence in the molecule of two azulene moieties substituted only in position 1 and a third azulene moiety substituted in both positions 1 and 3. The other signals in the spectrum are in accord with the proposed trimer structure for the product **7**.

The previous results pointed out the high reactivity of the 4′ position in the unsubstituted azulene-1-azoarenes; the less reactive 3 position participates to a small extent in the coupling and only with the 4′ position. Also, the higher ratio between 4,4′- and 3,4′-coupling for **2**, in comparison with **1a**, seems to indicate the increased coupling ability of the naphthyl group in comparison with phenyl.

Considering the relative reactivities of individual sites and the calculated electron densities and, also, the mechanism of the oxidative dimerization of aromatic compounds, the mechanism depicted in Scheme 3 can be suggested for the coupling
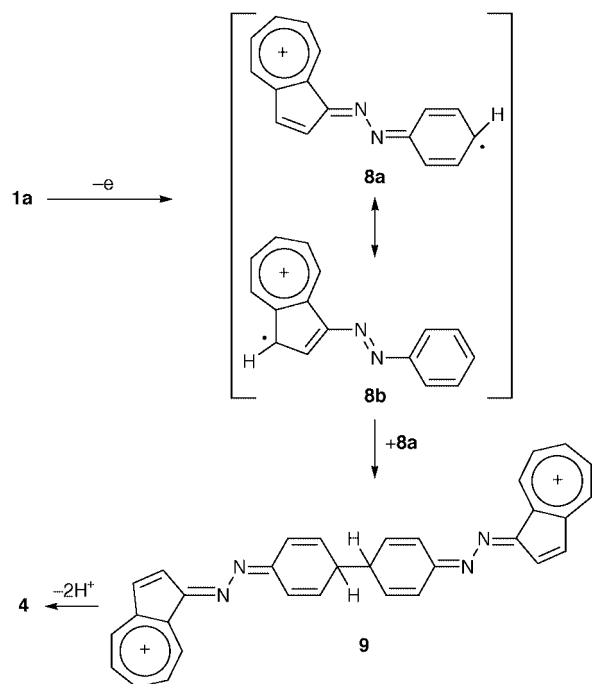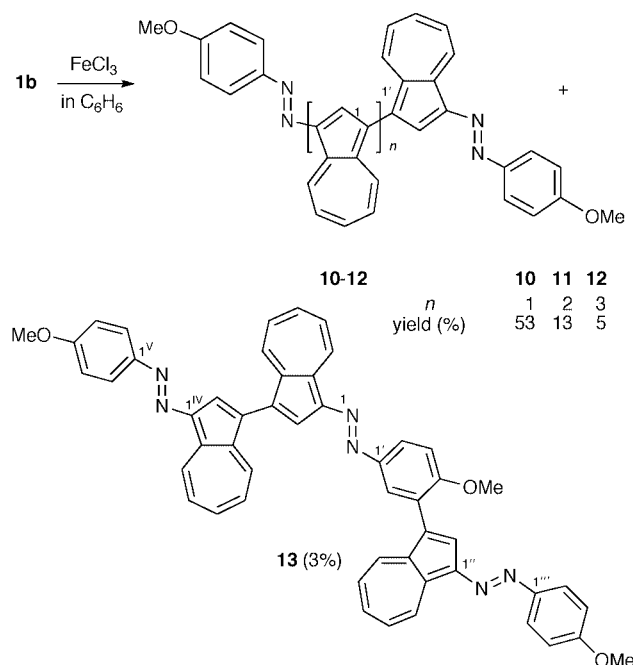

Scheme 3

discussed above. The first step in the oxidative coupling involves a single-electron transfer from the starting compound to FeCl$_3$ with the generation of the corresponding resonance stabilized radical cation **8**. The dication **9** must be generated[21] in the coupling reaction of two radical cations and the elimination of two protons affords the stable biphenyl product **4**.

The major coupling reaction in position 4′ (product **4** and **6**) is consistent with our calculations, which show that this position possesses the highest spin density in the radical cation (structure **8a**). The spin density in position 3 of the azulene is lower than in position 4′ and it is not high enough to lead to 3,3-coupling; therefore, only a 3,4′-coupling can be observed as a secondary reaction pathway. From the spin density calculations,[18] it transpires also that the difference between the spin density in the positions 4′ and 3 is higher for the radical cation containing naphthalene in comparison with those containing phenyl, and this explains the difference between the product ratio **4/5** and **6/7**.

Reaction of *para*-substituted azulene-1-azobenzenes

Astonishingly, in spite of the fact that position 3 participates in the mixed coupling with position 4′ for the above oxidations, no trace of products resulting from azulene–azulene coupling was found. It would be expected, however, that by appropriate substitution of the 4′ position in azulene-1-azobenzene, the oxidation could proceed with the coupling of the less reactive position in the radical cation, position 3 in the azulene moiety. To further test this hypothesis, some 4′ substituted azulene-1-azobenzenes were oxidized. From the four starting compounds investigated, only the oxidation of **1b** and **1c** takes place. The compound **1d** remained unchanged and **3** afforded, under severe reaction conditions (6 hours at 45 °C), only the 3-chloro-substituted product in 15% yield.

While the oxidation of the unsubstituted compounds **1a** and **2** gave only two products, the oxidation of **1b** yielded four products, in the yields reported in Scheme 4. They were separ-
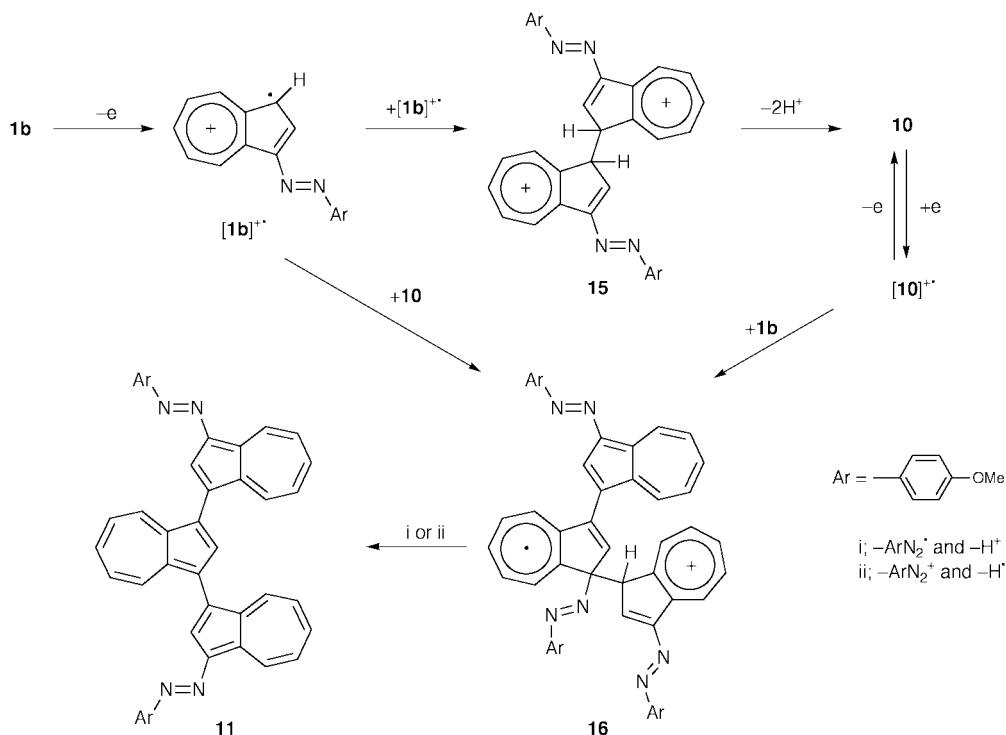

Scheme 4

ated by column chromatography (starting material conversion, 92%); traces of other products were also detected by TLC, however their separation and characterization failed.

In addition to unreacted starting material, **1b**, (3-chloro-azulene)-1-azo-(4′-methoxybenzene),[22] was separated in 0.5% yield as a low molecular weight compound.

For the main oxidation product, **10**, a dimeric structure can be suggested from the mass spectrum results ($m/z = 522$). From our computational results and the above described experiments, coupling at the 3 position of the two starting molecules could be expected. Indeed, the ^{1}H-NMR spectra show the almost unaltered AB spin system for the protons in *para*-substituted benzene both for the product, **10**, and for the starting material, **1b**, proving that the aromatic system does not participate in the reaction. The difference appears for the azulene proton signals. Thus, the two doublets for 2-H and 3-H in **1b** disappear and one singlet for two protons at δ 8.49 ppm (2-H and 2′-H) can be observed, supporting the 3,3′-coupling in the dimer **10**. The 3,3′-bis(azo)-1,1′-biazulene structure for **10** was unambiguously proved by the synthesis of this compound. Thus, by coupling an excess of diazonium chloride, obtained from *para*-anisidine, with 1,1′-biazulene,[23] compound **10** resulted in 10% yield, along with the mono azo coupled compound (61% yield).

Scheme 5

The ¹H-NMR spectrum of compound **11** shows the presence of two identical 1-(*p*-methoxyphenylazo)-azulen-3-yl groups with similar proton signals to those for the dimer **10**; in addition, one obtains also the signals characteristic for one 1,3-identically substituted azulene moiety (t, 7.08 ppm for 2 H, 5′-H and 7′-H, t, 7.55 ppm for 1 H, 6′-H, d, 8.42 ppm for 2 H, 4′-H and 8′-H and s, 8.27 for 1 H, 2′-H). Therefore, in **11** one azulene skeleton is 1,3-disubstituted with two 1-(*p*-methoxy-phenylazo)-azulen-3-yl substituents. The correctness of the proton assignments was attested by a COSY-90 experiment. The mass and ¹³C-NMR spectra and also the HETCOR experiment are in agreement with the proposed structure. Similar analytical arguments as for **11** were used for the structure assignment of compound **12** in which the 1,1′-biazulene moiety is 3,3′-substituted with two 1-(*p*-methoxyphenylazo)-azulen-3-yl substituents, indicating a remarkable structure with four azulenes coupled in the 1,3-positions.

The molecular weight resulting from the mass spectrum of the product **13** (*m/z* = 782) can be associated with a structure with three coupled starting molecules **1b**. However, the generation of a trimer was amazing because for the radical cation generated from **1b** the predicted reactive position in the coupling was position 3. Examination of the ¹H-NMR spectrum indicates the presence of two methoxy proton signals in the ratio 6:3 and two signals typical for the protons in position 2 in a 1,3-substituted azulene, in the ratio 2:1. These observations suggest a structure possessing two *p*-methoxy groups with almost the same neighbouring interactions and a different third group and, also, two similarly 1,3-substituted azulene moieties and one different. Two doublets of triplet signals in the aromatic field, each for four protons, indicate the presence of two similar *p*-methoxyphenylazo groups; for the third phenyl group the signals in ¹H- and ¹³C-NMR spectra are characteristic of a threefold substituted benzene. This means that the third *p*-methoxyphenylazo group is additionally coupled with an azulene moiety. The chemical shifts and coupling constants show that the new substituted position is vicinal to the methoxy group (δ 7.13 ppm, 1 H, d, *J* 8.8 Hz for *ortho* coupled 5′-H, δ 8.01 ppm, 1 H, dd, *J* 8.7 and 2.4 Hz for *ortho* and *meta* coupled 6′-H and δ 8.10 ppm, 1 H, d, *J* 2.4 Hz for *meta* coupled 2′-H). All the assignments were attested

by a COSY-90 experiment; the ¹³C-NMR spectrum is, also, in accord with the proposed structure.

The oxidation of azulene-1-azo-(4′-methylbenzene), **1c**, proceeded with the formation of a complex mixture of oligomers and a very small amount of 3,3-coupling dimeric product, **14**, was obtained. Compound **14** was separated by several column separations on alumina and it was contaminated with traces of oligomers. An important amount of oligomer mixture with poor solubility was also eluted as a fraction with a long retention time. It is interesting that in the ¹H-NMR spectrum of this mixture the CH₃ signal disappears. Some singlets can be observed, however, in the field of benzylic protons characteristic for di- and triphenylmethane. This remark, together with the poor yield in the dimer, suggests that under the reaction conditions the benzylic position in **1c** is also reactive.

The results for the oxidation of **1b** can be rationalized in terms of the mechanism proposed in Scheme 5.

As for the oxidation of unsubstituted azulene-1-azoarenes, the first reaction step is the generation of the radical cation [**1b**]˙⁺ by a single-electron transfer. The lower oxidation caused by electron-releasing substituents such as OCH₃ or CH₃ favours the increase of the radical cation concentration in the reaction medium. Together with the blocking of position 4′ this can explain the observed 3,3 coupling. In contrast, the electron-withdrawing action of NO₂ increases the oxidation potential and no such reaction occurs.

The intermediate [**1b**]˙⁺ can react in two different ways. The first possibility consists in the radical coupling of two such intermediates affording the dimeric dication **15** which, after the loss of two protons, leads to the product **10**. The fact that **10** is formed in more than 50% yield indicates this coupling as the main pathway for intermediate [**1b**]˙⁺. However, it is possible that, as for other simple azulene compounds,[10] the oxidation potential of the dimer **10** lies below that of the starting compound **1b** and in these conditions the generation of the dimeric radical cation, [**10**]˙⁺, can occur. The stability of both [**10**]˙⁺ and [**1b**]˙⁺ seems to be high enough to avoid an advanced reaction with aerial oxygen (the moderate oxidation yields may show, however, the formation of decomposition products). Two pathways are possible for the generation of the tris-1,3-coupled azulene compound **11**. The first consists in the alternative

consumption of the radical cation [1b]·+ in the attack towards 10 at the *ipso* position with the arylazo group. As a result, a new radical cation, 16, is formed. The same intermediate can result also from the reaction of 1b with [10]·+. After the loss of the *p*-methoxyphenylazo radical or cation and one proton or hydrogen atom, pathway (i) or (ii), respectively, the intermediate 16 gives the product 11. The product 12 can be obtained by the attack of the radical cation [1b]·+ on the product 11, by the radical coupling of two radical cations [10]·+ or by the reaction of 1b with radical cation [11]·+. The single-electron oxidation of the product 11 and 12 is also plausible with the generation of the corresponding radical cations, [11]·+ and [12]·+, however, the stability of these species hinders the subsequent reactions.

In summary we have found that the chemical oxidation of an azulene compound can proceed without damage to the azulene moiety if the substituent and the reaction conditions are adequately chosen. In the studied system which brings together an alternant and a non-alternant aromatic moiety, there is a reactivity sequence of the different positions in the molecule, predicted from the spin density calculations, which leads the reaction towards 4′,4′-, 3,4′- or 3,3-coupling of the starting azo compound. We expect that the extension of the reaction to systems with a C=N or C=C bond between the azulene and aromatic moieties will be favourable for the study of single-electron transfer oxidation. Our observations on the behaviour of azulene-1-azo-(4′-methylbenzene), 1c, prompted us to develop a study of benzyl substitution in such compounds after the blocking of the azulene reactive position 3. Both studies above discussed are in progress and will be subjects of future reports.

Experimental

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 2140B. UV spectra: Beckman DK-2A, UV 5240. ^{1}H- and ^{13}C-NMR spectra: Bruker WM 300, AC 300, ARX 300 and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz), *J* values are given in Hz, TMS was used as internal standard; when necessary, unequivocal signal assignment was confirmed by the analysis of the corresponding COSY and HETCOR spectra. Mass spectra: Finnigan MAT 311-A/100 MS. Column chromatography: basic alumina (activity BII-III (Brockmann)) or silica [70–230 mesh (ASTM)]. All eluted solutions were filtered before concentration. The dichloromethane (DCM) was distilled over calcium hydride, ethyl acetate over anhydrous sodium carbonate and trichloromethane was filtered on basic alumina.

General procedure for oxidation of azulene-1-azoarenes with ferric chloride

To a stirred solution of azo compound 1a–d, 2 or 3 (0.5 mmol), in benzene (12.5 cm³), anhydrous ferric chloride (324 mg, 2 mmol) was added at room temperature. The reaction was monitored by TLC (homogeneous samples were collected, washed with a saturated solution of sodium hydrogen carbonate and dried). The reaction was performed until the spot of the starting material had reached constant intensity (the reaction time will be specified below for each azo-compound). The reaction mixture was quenched with a saturated solution of sodium hydrogen carbonate and most of the benzene was evaporated under reduced pressure. The suspension was extracted with DCM (3 × 100 cm³), the organic extracts were washed with water, dried (Na₂SO₄), the solvent was evaporated under reduced pressure and the residue was separated by column chromatography.

The reaction of azulene-1-azobenzene, 1a. After stirring for 60 min and work-up, the residue was fractionated on alumina (column diameter (*d*) 20 mm and length (*l*) 500 mm) with benzene and five fractions were separated: *fraction 1* (5 mg), mixture of unidentified compounds (with a complicated ^{1}H-NMR spectrum); *fraction 2* (10 mg, 0.04 mmol), unreacted 1a, conversion 91%; *fraction 3* (4 mg, 0.09 mmol) dimer 4; *fraction 4* (17.5 mg, 0.03 mmol), trimer 5; *fraction 5* (17 mg), with ethyl acetate, slightly soluble powder (the ^{1}H-NMR spectrum suggests a mixture of oligomers).

Bis(azulene-1-azo)-4,4′-biphenyl, 4. Yield 38%, deep brown needles, mp 212–213 °C (benzene) (Found: C, 83.36; H, 4.83; N, 11.81. C₃₂H₂₂N₄ requires C, 83.09; H, 4.79; N, 12.11%); λ_{max}(dioxane)/nm 236 (log ε/dm³ mol⁻¹ cm⁻¹ 4.36), 240 (4.60), 284 (4.58), 337 (4.29) sh, 475 (4.83), 600 (3.49) sh, 660 (3.35) sh; δ_H(CDCl₃) 7.35 (2 H, t, *J* 9.7, 5″-H and 5‴-H), 7.47 (2 H, d, *J* 4.6, 3″-H and 3‴-H), 7.48 (2 H, t, *J* 9.8, 7″-H and 7‴-H), 7.78 (2 H, t, *J* 9.8, 6″-H and 6‴-H), 7.85 (4 H, d$_{AB}$, *J* 8.6, 2-H, 6-H, 2′-H and 6′-H), 8.10 (4 H, d$_{AB}$, *J* 8.5, 3-H, 5-H, 3′-H and 5′-H), 8.36 (2 H, d, *J* 10.0, 4″-H and 4‴-H), 8.37 (2 H, d, *J* 4.3, 2″-H and 2‴-H), 9.39 (2 H, d, *J* 9.8, 8″-H and 8‴-H); δ_C(CDCl₃) 120.13, (t, C-3″ or C-7″), 122.76 (t, C-3 and C-5), 125.23 (t, C-2″), 126.59 (t, C-7″ or C-3″), 126.66 (t, C-5″), 127.58 (t, C-4 and C-6), 135.52 (t, C-8″), 138.48 (t, C-4″), 138.80 (q), 139.56 (t, C-6″), 141.09 (q), 144.02 (q), 144.21 (q), 153.50 (q); *m/z*(70 eV) 463 (M⁺ + 1, 5%), 462 (M⁺, 38), 461 (M⁺ − 1, 14), 232 (23), 231 (½M²⁺, 5), 184 (7), 155 (C₁₀H₇N₂⁺, 15), 143 (24), 127 (C₁₀H₇⁺, 100).

Bis[4′-(azulene-1-azophenyl)]-3,4′-(azulene-1-azobenzene), 5. Yield 17%, deep brown microcrystalline powder, mp 238–241 °C (with decomp., from trichloromethane and precipitation with *n*-pentane) (Found: C, 82.90; H, 5.09; N, 12.01. C₄₈H₃₂N₆ requires C, 83.21; H, 4.66; N, 12.13%); λ_{max}(DCM, very slightly soluble, ultrasound treatment)/nm 281, 332 sh, 490; δ_H(CDCl₃) 7.39 (2 H, t, *J* 9.7, 5‴-H and 5^V-H), 7.44 (1 H, t, *J* 9.6, 5-H), 7.48 (5 H, complex m, 7-H, 7‴-H, 7^V-H, 3‴-H and 3^V-H), 7.82 (3 H, t, *J* 10.0, 6-H, 6‴-H and 6^V-H), 7.86 (2 H, d, *J* 8.2, 3′-H and 5′-H or 3″-H and 5″-H or 3^{IV}-H and 5^{IV}-H), 7.93 (2 H, d, *J* 8.6, 3′-H and 5′-H or 3″-H and 5″-H or 3^{IV}-H and 5^{IV}-H), 7.94 (2 H, d, *J* 8.5, 3′-H and 5′-H or 3″-H and 5″-H or 3^{IV}-H and 5^{IV}-H), 8.09 (2 H, d, *J* 8.5, 2′-H and 6′-H or 2″-H and 6″-H or 2^{IV}-H and 6^{IV}-H), 8.13 (2 H, d, *J* 7.9, 2′-H and 6′-H or 2″-H and 6″-H or 2^{IV}-H and 6^{IV}-H), 8.16 (2 H, d, *J* 8.2, 2′-H and 6′-H or 2″-H and 6″-H or 2^{IV}-H and 6^{IV}-H), 8.33 (1 H, d, *J* 4.6, 2‴-H or 2^V-H), 8.35 (1 H, d, *J* 4.6, 2^V-H or 2‴-H), 8.44 (2 H, d, *J* 9.2, 4‴-H and 4^V-H), 8.52 (1 H, s, 2-H), 8.74 (1 H, d, *J* 9.6, 4-H), 9.39 (1 H, d, *J* 9.8, 8‴-H or 8^V-H), 9.41 (1 H, d, *J* 9.7, 8^V-H or 8‴-H), 9.47 (1 H, d, *J* 9.8, 8-H); *m/z*(FD 0–20 mA) 696 (M⁺ + 4, 16%), 695 (M⁺ + 3, 17), 694 (M⁺ + 2, 53), 693 (M⁺ + 1, 54), 692 (M⁺, 100), 522 (27), 346 (33); *m/z*(70 eV) 372 (13%), 323 (34), 184 (40), 143 (73), 127 (100), 115 (33).

The reaction of azulene-1-azo-1′-naphthalene, 2. After a reaction time of 3 h and work-up, the residue was separated on silica (*d* 20 mm, *l* 500 mm) with DCM–*n*-pentane (1 : 1) and five fractions were collected: *fraction 1* (3 mg), a complex mixture of unidentified compounds (from ^{1}H-NMR spectrum); *fraction 2* (30 mg, 0.11 mmol), unreacted 2, conversion 77%; *fraction 3* (9 mg, 17 mmol), dimer 6; *fraction 4* (8 mg, 0.01 mmol), trimer 7; *fraction 5* (2 mg), with ethyl acetate, slightly soluble powder (the ^{1}H-NMR spectrum suggests a mixture of oligomers).

4,4′-Bis(1-azuleneazo)-(1,1′-binaphthalene), 6. Yield 88%, black microcrystalline powder, mp 278–280 °C (from DCM on precipitation with *n*-pentane) (Found: C, 85.13; H, 4.89; N, 9.88. C₄₀H₂₆N₄ requires C, 85.38; H, 4.66; N, 9.96%); λ_{max}(dioxane, very slightly soluble, ultrasound treatment)/nm 286, 330 sh, 471; δ_H(CDCl₃) 7.37 (2 H, t, *J* 9.6, 5″-H and 5‴-H), 7.41 (2 H, t, *J* 9.1, 7″-H and 7‴-H), 7.51 (2 H, d, *J* 7.7, 8-H and 8′-H), 7.52 (2 H, d, *J* 4.5, 3″-H and 3‴-H), 7.57 (2 H, t, *J* 8.3, 6-H and 6′-H), 7.66 (2 H, t, *J* 8.2, 7-H and 7′-H), 7.68 (2 H, d$_{AB}$, *J* 7.6, 3-H and 3′-H), 7.79 (2 H, t, *J* 9.9, 6″-H and 6‴-H), 8.15 (2 H, d$_{AB}$, *J* 7.7, 2-H and 2′-H), 8.39 (2 H, d, *J* 9.3, 4″-H and

4‴-H), 8.56 (1 H, d, *J* 4.5, 2″-H and 2‴-H), 9.20 (2 H, d, *J* 8.2, 5-H and 5′-H), 9.49 (2 H, d, *J* 9.9, 8″-H and 8‴-H); *m/z*(70 eV): 564 (M⁺ + 2, 2%), 563 (M⁺ + 1, 11), 562 (M⁺, 25), 561 (M⁺ − 1, 3), 155 (16), 143 (44), 127 (C₇H₁₀⁺, 100).

3,4′-Bis[azulene-1-azo-1′-(4′-naphthyl)](azulene-1-azo-1′-naphthalene), 7. Yield 7%, black microcrystalline powder, mp 204–207 °C (from DCM on precipitation with *n*-pentane) (Found: C, 85.28; H, 4.84; N, 9.88. C₆₀H₃₈N₆ requires C, 85.49; H, 4.54; N, 9.97%); λₘₐₓ(dioxane, very slightly soluble, ultrasound treatment)/nm 284, 332, 481; δ_H(CDCl₃) 7.22 to 7.84 (m, 22 H, protons with the unassigned structure), 7.93 (1 H, d, *J* 8.5, 2^IV-H or 5^IV-H), 8.17 (1 H, d, *J* 7.9, 2″-H or 3′-H or 3^IV-H), 8.19 (1 H, d, *J* 7.8, 2″-H or 3′-H or 3^IV-H), 8.22 (1 H, d, *J* 7.6, 2″-H or 3′-H or 3^IV-H), 8.25 (1 H, d, *J* 10.4, 4-H), 8.38 (2 H, d, *J* 9.3, 4‴-H and 4^V-H), 8.55 (1 H, d, *J* 4.4, 2‴-H or 2^V-H), 8.57 (1 H, d, *J* 4.3, 2^V-H or 2‴-H), 8.76 (1 H, s, 2-H), 9.20 (2 H, d, *J* 8.5, 8′-H and 5″-H), 9.24 (1 H, d, *J* 8.8, 8^IV-H), 9.49 (2 H, d, *J* 9.9, 8‴-H and 8^V-H), 9.62 (1 H, d, *J* 9.8, 8-H); *m/z*(FD 0–25 mA) 846 (M⁺ + 4, 5%), 865 (M⁺ + 3, 26), 844 (M⁺ + 2, 50), 843 (M⁺ + 1, 85), 842 (M⁺, 100), 705 (47), 704 (60), 703 (47), 421 (42); *m/z*(70 eV) 432 (10%), 284 (27), 143 (100), 127 (C₁₀H₇⁺, 30), 115 (45).

The reaction of azulene-1-azo-(4′-methoxybenzene), 1b. After 2 h of stirring and work-up, the solution was concentrated under reduced pressure to 10 cm³, 20 cm³ *n*-pentane was added and the obtained suspension was filtered to give a precipitate and a filtrate. The precipitate was separated on silica (*d* 30 mm and *l* 500 mm) with DCM–*n*-pentane (20 : 1) and seven fractions were collected: *fraction 1* (23 mg), viscous liquid mixture of products; *fraction 2* (4 mg), compound **11**; *fraction 3* (13 mg) mixture of compound **11**, 64% (molar, from ¹H-NMR signal integrals) and dimer **10**, 36%; *fraction 4* (55 mg), dimer **10**; *fraction 5* (4 mg), dimer **10** as major compound (from ¹H-NMR signal integrals), the fractions 2–5 together contain 12.5 mg (0.02 mmol) compound **11**, and 63.5 mg (0.12 mmol) dimer **10**; *fraction 6* (3 mg) unidentified mixture of compounds (complicated ¹H-NMR spectrum); *fraction 7* (4 mg, 0.005 mmol), trimer **13**. The fraction 1 together with the filtrate were evaporated under reduced pressure, the residue was separated on silica (*d* 30 mm, *l* 500 mm) with DCM–*n*-pentane (5 : 1) and five fractions were collected: *fraction 1* (7 mg), mixture of several compounds (complicated ¹H-NMR spectrum); *fraction 2* (3 mg, 0.01 mmol), 3-chloroazulene-1-azo-(4′-methoxybenzene),[17] yield 2%; *fraction 3* (10 mg, 0.038 mmol), unreacted **1b**, conversion 92%; *fraction 4* (5 mg), unidentified mixture; *fraction 5* (4 mg, 0.005 mmol), compound **12**.

3,3′-Bis(4-methoxyphenylazo)-(1,1′-biazulene), 10. Yield 53%, reddish-brown microcrystalline powder, mp 298.5–300 °C (DCM, with slight decomp.) (Found: C, 78.24; H, 5.23; N, 10.83. C₃₄H₂₆N₄O₂ requires, C, 78.14; H, 5.01; N, 10.74%); λₘₐₓ(dioxane)/nm 241 (log ε 4.52), 275 (4.47) sh, 294 (4.51), 344 (4.26), 420 (4.49) sh, 442 (4.50), 612 (3.29) sh; δ_H(CDCl₃, slightly soluble) 3.90 (6 H, s, 2 OCH₃), 7.04 (4 H, dt_AB, *J* 9.0 and 2.0, (*o*-OCH₃)-H), 7.24 (2 H, t, *J* 9.8, 7-H), 7.41 (2 H, t, *J* 9.8, 5-H), 7.72 (2 H, t, *J* 10.0, 6-H), 8.00 (4 H, dt_AB, *J* 9.0 and 3.0, (*m*-OCH₃)-H), 8.45 (2 H, d, *J* 9.4, 8-H), 8.49 (2 H, s, 2-H), 9.38 (2 H, d, *J* 9.8, 4-H); δ_H(*d₈*-THF) 3.95 (6 H, s, 2 OCH₃), 7.13 (4 H, dt_AB, *J* 9.0 and 2.0, (*o*-OCH₃)-H), 7.38 (2 H, t, *J* 10.1, 7-H), 7.52 (2 H, t, *J* 9.9, 5-H), 8.89 (2 H, t, *J* 10.0, 6-H), 8.06 (4 H, dt_AB, *J* 9.0 and 2.3, (*m*-OCH₃)-H), 8.54 (2 H, d, *J* 9.3, 8-H), 8.55 (2 H, s, 2-H), 9.47 (2 H, d, *J* 9.6, 4-H); δ_C(*d₈*-THF) 55.7 (s, OCH₃), 114.9 (t, aryl-*C*H), 124.6 (t, aryl-*C*H), 126.4 (t), 126.9 (t), 127.3 (t), 127.4 (q), 136.3 (t), 138.4 (t), 139.5 (q), 141.1 (t), 141.9 (q), 144.0 (q), 149.5 (q), 162.2 (q); *m/z*(FD 0–20 mA) 524 (M⁺ + 2, 5%), 523 (M⁺ + 1, 30), 522 (M⁺, 100); *m/z*(70 eV) 522 (M⁺, >1%), 123 (67), 108 (100), 80 (50).

3,3″-Bis(4-methoxyphenylazo)-(1,1′ : 3′,1″-terazulene), 11. Yield 13%, microcrystalline brown powder with green sheen, mp 136–137 °C (trichloromethane) (Found: C, 81.20; H, 5.01;

N, 8.51. C₄₄H₃₂N₄O₂ requires C, 81.46; H, 4.97; N, 8.64%); λₘₐₓ(dioxane)/nm 246 (log ε 4.64), 284 (4.67), 302 (4.67), 403 (4.69), 466 (4.55) sh, 605 (3.21) sh; δ_H(CDCl₃) 3.84 (6 H, s, 2 OCH₃), 6.98 (4 H, dt_AB, *J* 9.0 and 2.1, (*o*-OCH₃)-H), 7.08 (2 H, t, *J* 9.9, 5′-H and 7′-H), 7.13 (2 H, t, *J* 9.7, 7-H and 7″-H), 7.32 (2 H, t, *J* 9.9, 5-H and 5″-H), 7.55 (1 H, t, *J* 9.7, 6′-H), 7.64 (2 H, t, *J* 9.7, 6-H and 6″-H), 7.95 (4 H, dt_AB, *J* 9.0 and 2.1, (*m*-OCH₃)-H), 8.27 (1 H, s, 2′-H), 8.40 (2 H, d, *J* 9.3, 8-H and 8″-H), 8.42 (2 H, d, *J* 9.4, 4′-H and 8′-H), 8.49 (2 H, s, 2-H and 2″-H), 9.32 (2 H, d, *J* 9.7, 4-H and 4″-H); δ_C(CDCl₃) 55.7 (s, OCH₃), 114.3 (t, (*o*-OCH₃)-*C*H), 123.9 (t, C-5′ and C-7′), 124.0 (t, (*m*-OCH₃)-*C*H), 124.8 (q), 125.6 (t, C-2 and C-2″), 126.1 (t, C-6 and C-6′), 126.3 (t, C-7 and C-7″), 127.9 (q), 135.8 (t, C-4 and C-4″), 136.8 (t, C-4′ and C-8′), 137.9 (t, C-8 and C-8″), 138.4 (q), 139.1 (q), 139.4 (t, C-6′), 139.7 (t, C-2′), 140.2 (t, C-6 and C-6″), 141.1 (q), 143.2 (q), 148.7 (q), 160.9 (q); *m/z*(70 eV) 650 (M⁺ + 2, >1%), 649 (M⁺ + 1, >1), 648 (M⁺, 1.5), 647 (M⁺ − 1, >1), 555 (>1), 123 (70), 108 (100), 80 (45).

3,3‴-Bis(4-methoxyphenylazo)-(1,1′ : 3′,1″ : 3″,1‴-quater-azulane), 12. Yield 5%, black powder, not definite mp (Found: C, 82.78; H, 5.02; N, 7.10. C₅₄H₃₈N₄O₂ requires C, 83.71; H, 4.94; N, 7.23%); λₘₐₓ(DCM)/nm 237 (log ε 4.34), 263 (4.30), 290 (4.20), 350 (4.20), 407 (4.27), 465 (4.09) sh, 600 (2.86) sh; δ_H(CDCl₃) 3.91 (6 H, s, 2 OCH₃), 7.06 (4 H, dt_AB, *J* 9.0 and 2.5, (*o*-OCH₃)-H), 7.11 (2 H, t, *J* 9.8, 5′-H and 5″-H or 7′-H and 7″-H), 7.12 (2 H, t, *J* 9.8, 7′-H and 7″-H or 5′-H and 5″-H), 7.21 (2 H, t, *J* 9.8, 7-H and 7‴-H), 7.40 (2 H, t, *J* 9.7, 5-H and 5‴-H), 7.60 (2 H, t, *J* 9.7, 6′-H and 6″-H), 7.71 (2 H, t, *J* 9.8, 6-H and 6‴-H), 8.03 (4 H, dt_AB, *J* 9.0 and *J* 2.5, (*m*-OCH₃)-H), 8.43 (2 H, s, 2′-H and 2″-H), 8.49 (2 H, d, *J* 10.2, 4′-H and 4″-H or 8′-H and 8″-H), 8.52 (2 H, d, *J* 9.8, 8-H and 8‴-H), 8.54 (2 H, d, *J* 9.4, 8′-H and 8″-H or 4′-H and 4″-H), 8.59 (2 H, s, 2-H and 2‴-H), 9.40 (2 H, d, *J* 9.8, 4-H and 4‴-H); *m/z*(FD 10–15 mA) 778 (M⁺ + 4, 7%), 777 (M⁺ + 3, 20), 776 (M⁺ + 2, 60), 775 (M⁺ + 1, 100), 686 (8), 685 (20), 684 (22), 683 (41).

3,3′-Bis[(4-methoxybenzene)-1-azo-1′-azulen-3′-yl][azulene-1-azo-1′-(4′-methoxybenzene)], 13. Yield 3%, deep brown microcrystalline powder, mp 154–156 °C (trichloromethane, with slight decomp.) (a pure sample for elemental analysis could not be obtained); λₘₐₓ(dioxane)/nm 241 (log ε 4.67), 293 (4.69), 346 (4.64), 425 (4.73) sh, 442 (4.74), 465 (4.72) sh, 605 (3.30) sh; δ_H(CDCl₃) 3.81 (3 H, s, 4′-OCH₃), 3.83 (6 H, s, 4‴-OCH₃ and 4^IV-OCH₃), 6.97 (4 H, dt_AB, *J* 8.9 and 2.0, 3‴-H, 5‴-H, 3^V-H and 5^V-H), 7.13 (1 H, d, *J* 8.8, 5′-H), 7.16 (1 H, t, *J* 9.5, 5-H or 5^IV-H), 7.17 (1 H, t, *J* 9.6, 5^IV-H or 5-H), 7.19 (1 H, t, *J* 9.7, 5″-H), 7.31 (1 H, t, *J* 9.6, 7″-H), 7.34 (1 H, t, *J* 9.6, 7-H or 7^IV-H), 7.35 (1 H, t, *J* 9.8, 7^IV-H or 7-H), 7.64 (1 H, t, *J* 9.7, 6″-H), 7.65 (2 H, t, *J* 10, 6-H and 6^IV-H), 7.93 (4 H, dt_AB, *J* 8.9 and 2.0, 2‴-H, 6‴-H, 2^V-H and 6^V-H), 8.01 (1 H, dd, *J* 8.7 and 2.4, 6′-H), 8.10 (1 H, d, *J* 2.4, 2′-H), 8.26 (1 H, d, *J* 9.4, 4″-H), 8.39 (1 H, d, *J* 9.4, 4-H or 4^IV-H), 8.40 (1 H, d, *J* 10.0, 4^IV-H or 4-H), 8.42 (2 H, s, 2-H and 2^IV-H), 8.44 (1 H, s, 2″-H), 9.29 (1 H, d, *J* 9.5, 8-H or 8″-H or 8^IV-H), 9.31 (1 H, d, *J* 9.5, 8-H or 8″-H or 8^IV-H), 9.32 (1 H, d, *J* 9.0, 8-H or 8″-H or 8^IV-H); δ_C(CDCl₃) 55.7 (s, OCH₃), 56.1 (s, OCH₃), 111.3 (t), 114.3 (t), 123.9 (t), 124.0 (t), 124.7 (t), 125.0 (t), 125.6 (t), 126.1 (t), 126.3 (t), 126.5 (t), 126.7 (t), 126.8 (q), 128.8 (q), 135.6 (t), 135.8 (t), 136.0 (t), 137.8 (t), 139.0 (q), 139.1 (q), 139.8 (t), 140.4 (t), 141.2 (q), 142.8 (q), 143.1 (q), 148.3 (q), 148.6 (q), 148.7 (q), 158.6 (q), 160.8 (q), 161.0 (q); *m/z*(FD 0–20 mA) 785 (M⁺ + 3, 10%), 784 (M⁺ + 2, 23), 783 (M⁺ + 1, 82), 782 (M⁺, 100), 392 (19), 391 (17).

The reaction of azulene-1-azo-(4′-methylbenzene), 1c. After 4 h of stirring and work-up, the residue was separated by chromatography on alumina (*d* 20 mm, *l* 300 mm) and two fractions were collected: *fraction 1* (17 mg), eluted with DCM–*n*-pentane (1 : 1), containing the dimer **14**, and *fraction 2* (40 mg), eluted with DCM (a large amount was used). The ¹H-NMR spectrum

of a diluted solution of the *fraction 2* in CDCl$_3$ and also in CD$_2$Cl$_2$ was very complicated in the aromatic field; the CH$_3$ signal at 2.45 ppm for **1c** disappeared and some singlet signals could be observed in the field between 4 and 6 ppm. All attempts at purification of the product **14** from the *fraction 1*, by repeated chromatographic separations on alumina or silica and crystallization, failed (in the ^{1}H-NMR spectrum, some signal traces of insignificant quantities of compounds were observed).

3,3′-Bis(4-methylphenylazo)(1,1′-biazulene), **14**. Black powder (a pure sample for elemental analysis could not be obtained); δ_H(CDCl$_3$) 2.45 (6 H, s, C*H*$_3$), 7.27 (2 H, t, *J* 9.9, 5-H), 7.33 (4 H, d$_{AB}$, *J* 8.1, 3′-H and 5′-H), 7.45 (t, *J* 9.6, 2 H, 7-H), 7.75 (2 H, t, *J* 9.8, 6-H), 7.92 (4 H, d$_{AB}$, *J* 8.2, 2′-H and 6′-H), 8.48 (2 H, d, *J* 9.2, 8-H), 8.51 (2 H, s, 2-H), 9.42 (2 H, d, *J* 9.2, 4-H); *m/z*(70 eV) 492 (M$^+$ + 2, 3%), 491 (M$^+$ + 1, 8), 490 (M$^+$, 32), 489 (M$^+$ − 1, 100), 488 (M$^+$ − 2, 73), 387 (18), 250 (21), 106 (26), 97 (23).

The reaction of 4,6,8-trimethylazulene-1-azo-(4′-methoxybenzene), 3. After 6 h of stirring at 45 °C and usual work up, the residue was separated on silica with DCM–*n*-pentane (1:1) and the chlorinated product was separated as the first fraction (14 mg, 0.041 mmol). By elution with DCM the unreacted azo compound **3** was collected (70 mg, 0.23 mmol), conversion 46%.

(3-Chloro-4,6,8-trimethylazulene)-1-azo-(4′-methoxybenzene). 15% yield, deep green crystals, mp 116–117 °C (*n*-hexane) (Found: C, 70.43; H, 5.80; N, 8.30; Cl, 10.13. C$_{20}$H$_{19}$N$_2$OCl requires C, 70.89; H, 5.65; N, 8.27; Cl, 10.46%); δ_H(CDCl$_3$) 2.58 (3 H, s, 6-C*H*$_3$), 3.17 (3 H, s, 4-C*H*$_3$), 3.30 (3 H, s, 8-C*H*$_3$), 3.89 (3-H, s, OC*H*$_3$), 7.01 (2 H, dt$_{AB}$, *J* 8.9 and 2.0, 3′-H and 5′-H), 7.02 (1 H, s, 5-H), 7.13 (1 H, s, 7-H), 7.83 (2 H, dt$_{AB}$, *J* 9 and 2.1, 2′-H and 6′-H), 8.02 (1-H, s, 2-H); δ_C(CDCl$_3$) 29.7, 30.3 and 30.8 (s, *C*H$_3$-4, 6 and 8), 55.5 (s, O*C*H$_3$), 103.3 (t), 114.2 (t, C-3′ and C-5′), 120.5 (q), 123.35 (q), 124.0 (t, C-2′ and C-6′), 132.0 (q), 132.2 (q), 132.5 (t), 133.0 (t), 148.4 (q), 148.7 (q), 149.4 (q), 149.5 (q), 160.6 (q).

The coupling of the biphenyl-4,4′-bis(diazonium) dichloride with azulene

To a stirred solution of the bis-diazonium dichloride prepared from benzidine dichloride (460 mg, 2 mmol), aqueous 37% HCl (0.6 cm^3) and sodium nitrite (140 mg, 2 mmol) in water (8 cm^3), at 0 °C, a solution of azulene (538 mg, 4.2 mmol) and sodium acetate (600 mg) in ethanol (40 cm^3) was slowly added and the reaction mixture was stirred for 30 min at room temperature. The ethanol was evaporated under reduced pressure and the residue was extracted with benzene (2 × 40 cm^3). The organic solution was washed with water and dried (Na$_2$SO$_4$). The chromatographic separation of the residue on alumina with *n*-pentane–benzene (10:1) gave compound **4** (720 mg, 78%); azulene (20 mg) was collected as first fraction. The physical parameters and NMR spectra are identical with those of compound **4** separated in the oxidation of **1a**.

The coupling of 4-methoxyphenyldiazonium chloride with 1,1′-biazulene

A solution of 4-methoxyphenyldiazonium chloride, prepared at 0 °C from 4-methoxyaniline (240 mg, 1.94 mmol), aqueous 37% HCl (0.6 cm^3) and sodium nitrite (133 mg, 1.94 mmol) in water (8 cm^3), was added slowly to a stirred solution of 1,1′-biazulene (200 mg, 0.79 mmol)^{23} and sodium acetate (610 mg) in ethanol (40 cm^3). After stirring at room temperature for one hour and work-up, the crude material was separated on alumina (*d* 30 mm, *l* 200 mm), with benzene–*n*-pentane (1:1), *fraction 1* (40 mg, 0.16 mmol), unreacted biazulene; *fraction 2* (150 mg, 61%), 3-(*p*-methoxyphenylazo)-1,1′-biazulene; *fraction 3* (33 mg), containing as major component the dimer **10** (from the

^{1}H-NMR); *fraction 4* (19 mg), dimer **10**. The spectra and the physical parameters are the same with those of the dimer separated in the oxidation of **1b**.

3-(4-Methoxyphenylazo)-1,1′-biazulene. Brown needles, mp 131 °C (benzene, decomp.) (Found: C, 83.18; H, 5.37; N, 7.19. C$_{27}$H$_{20}$N$_2$O requires C, 83.47; H, 5.19; N, 7.21%); λ_{max}(*n*-hexane)/nm 242 (log ε 4.47), 267 (4.50), 296 (4.48), 388 (4.35), 600 (2.93); δ_H(CDCl$_3$) 3.89 (3 H, s, OC*H*$_3$), 7.02 (2 H, d$_{AB}$, *J* 9.1, (*o*-OCH$_3$)-H), 7.08 (1 H, t, *J* 9.7, 5′-H), 7.11 (1 H, t, *J* 9.2, 7′-H), 7.14 (1 H, t, *J* 9.9, 7-H), 7.32 (1 H, t, *J* 9.6, 5-H), 7.51 (1 H, d, *J* 3.8, 3′-H), 7.56 (1 H, t, *J* 9.2, 6′-H), 7.62 (1 H, t, *J* 9.9, 6-H), 8.00 (2 H, d$_{AB}$, *J* 8.9, (*m*-OCH$_3$)-H), 8.09 (1 H, d, *J* 3.8, 2′-H), 8.32 (1 H, d, *J* 10.4, 4′-H), 8.35 (1 H, d, *J* 10.5, 8′-H), 8.41 (1 H, d, *J* 9.9, 8-H), 8.47 (1 H, s, 2-H), 9.34 (1 H, d, *J* 9.9, 4-H).

Acknowledgements

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