Synthesis and Properties of *syn*-[2.2](1,6)- and (4,6)Azulenophanes and Macrocyclic Azulenophanes

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A regioselective synthesis of *syn*-[2.2](1,6)azulenophane (**9**) and *syn*-[2.2](4,6)azulenophane (**12**) is described. Azulenophane **9** is prepared by deprotonation of 1,2-bis(6-methylazulen-1-yl)ethane (**5**), followed by oxidative coupling of the initially formed dilithium salt **8** with iodine under high-dilution conditions in 17 % yield, along with the macrocyclic [2.2.2.2](1,6)azulenophane (**10**) (3 %), and [2.2.2.2.2.2] (1,6)azulenophane (**11**) (1.5 %). The azulenophane **12** and the macrocyclic [2.2.2.2](4,6)azulenophane (**13**) are obtained by coupling of the dianion of 1,2-bis(4-methylazulen-6-yl)-ethane (**14**). The structural assignments of the title compounds are based on their spectral data. Protonation of **9** furnishes the mono- and dications **24** and **25**, respectively, of which the first exhibits a charge-transfer band in its electronic spectrum, indicating a transannular interaction between the protonated and unprotonated azulene units. Protonation of **12** yields the mono- and dications **26** and **27**, respectively. In contrast to **24**, no new band due to an intramolecular transannular charge-transfer interaction is observed in the electronic spectrum of **26**, and this is due to an insufficient overlap between the protonated and unprotonated azulene decks in **26**. Vilsmeier formylation of **9** with 1.5 mol equivalents of phosphoryl chloride in DMF at room temp. yields 3-formyl-*syn*-[2.2](1,6)azulenophane (**28**) in 15 % yield. Under the same reaction conditions a double formylation of **9** with 3 mol equivalents of phosphoryl chloride leads to 3,3′-diformyl-*syn*-[2.2](1,6)azulenophane (**29**) in 42 % yield. The aminomethylation of **9** with paraformaldehyde and *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane in the presence of acetic acid furnishes the Mannich bases 3-*N*,*N*-dimethylaminomethyl-*syn*-[2.2](1,6)azulenophane (**30**) and 3,3′-bis(*N*,*N*-dimethylaminomethyl)-*syn*-[2.2](1,6)azulenophane (**31**) in 40 % and 46 % yields, respectively.

Azulenophanes are of great interest due to their specific physical and chemical properties, since two azulene nuclei are rigidly positioned on top of one another in a parallel fashion; the dipolar character of the azulene system is suitable for an investigation of transannular interactions[1]. Furthermore, the azulenophanes should be versatile ligands for new transition metal complexes, especially those with columnar structures with the potential for conductivity. Finally, ring enlargement reactions[2] of the azulenophanes with dimethyl acetylenedicarboxylate to give heptalenophanes may be an attractive goal. For these purposes, efficient syntheses of azulenophanes are required. However, all syntheses of azulenophanes, like *syn*- and *anti*-[2.2](2,6)azulenophanes, described to date in the literature yield a mixture of *syn* and *anti* isomers only on a milligram scale[1][3][4][5], and their separation can be tedious. Therefore, we have developed a new approach for the regioselective synthesis of some *syn*- and *anti*-azulenophanes.

The 1,8-Hofmann elimination of 2-methylazulene functionalized at position 6 with a trialkylammonium methyl group[1][3], or 6-methylazulene functionalized at position 2 with a trialkylammonium methyl group[4][5], afforded [2.2](2,6)azulenophanes as a mixture of the *syn* and *anti* isomers, but the *syn*- and *anti*-[2.2](1,6)azulenophanes could not be obtained by this reaction with corresponding 1,6-disubstituted azulenes.[5] Koenig et al. used a fluoride-induced 1,7-elimination of 1-trimethylsilylmethyl-6-trialkylammoniummethylazulene or 6-trimethylsilylmethyl-1-trialkylammoniummethylazulene to obtain the *anti*-[2.2](1,6)azulenophane[6], but so far the *syn*-[2.2](1,6)azulenophane (**9**) remains unknown. Furthermore, [2.2](4,6)azulenophanes, like *syn*-[2.2](4,6)azulenophane (**12**), are also most attractive compounds because they would provide a new entry to the synthesis of novel polycyclic hydrocarbons by intramolecular transannular coupling reactions, as in the case of [2.2]metacyclophane[7], [2.2](1,3)azulenometacyclophane[8], and [2.2](1,3)azulenophane[9]. There has not been any report to date on the synthesis of this class of compounds. Finally, macrocyclic azulenophanes, such as [2.2.2.2](1,6)azulenophane (**10**), [2.2.2.2.2.2](1,6)azulenophane (**11**), and [2.2.2.2](4,6)azulenophane (**13**), have been inaccessible until now. It would be expected that these systems form well-defined polar host cavities for inclusion of certain guest molecules due to the incorporation of polar azulene units in the macrocycles, and therefore may be of interest in "Host−Guest Chemistry"[10]. Only one synthesis of a representative of this class of macrocyclic phanes is known so far[11]. Here we report the successful synthesis of

the azulenophanes **9**−**13** and describe some of their properties.[12]

Synthesis

Synthesis of syn-[2.2](1,6)Azulenophane (**9**): Preliminary studies in our laboratory indicated that the oxidative coupling reaction of lithium 6-azulenemethide (**2**), generated by deprotonation of 6-methylazulene (**1**) with lithium diisopropylamide (LDA), affords 1,2-bis(azulen-6-yl)ethane (**3**) in good yield (Scheme 1)[13]. This reaction sequence also allows a regioselective synthesis of *syn*-[2.2](1,6)azulenophane (**9**) by an intramolecular oxidative coupling reaction of deprotonated 1,2-bis(6-methylazulen-1-yl)ethane (**5**), as shown in Scheme 2.

Scheme 1
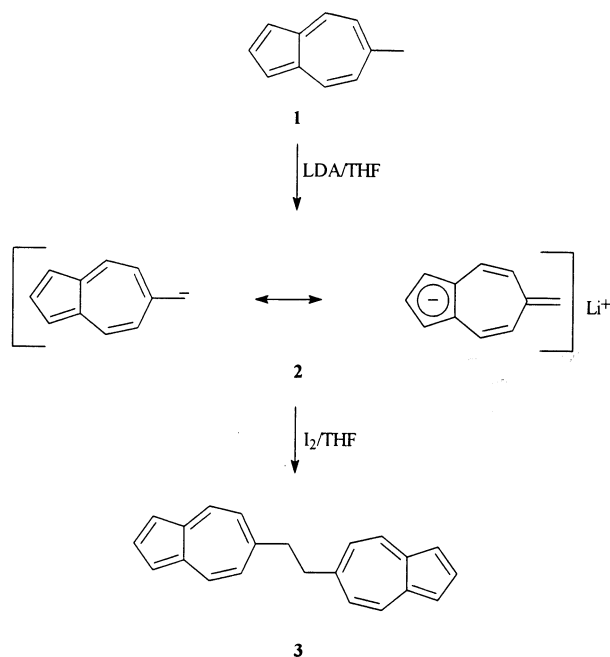
The reductive coupling reaction of the quaternary ammonium salt **4**[5] with zinc in DMF, using a similar procedure to that described by Murata et al.[11], afforded three products which could be separated by chromatography. In addition to 15% of the known 1,6-dimethylazulene (**6**)[6][14], 43% of the desired bisazulenylethane **5** was obtained as blue prisms. The third product (8%), isolated as blue plates, was identified as 1-(6-methylazulen-1-yl)methyl-3-(6-methylazulen-1-yl)ethyl-6-methylazulene (**7**).

1,2-Bis(6-methylazulen-1-yl)ethane (**5**) was smoothly deprotonated with LDA in THF at room temp. to give the resonance stabilized dilithium salt **8** which, by an intermolecular oxidative coupling reaction with iodine at −80°C under high-dilution conditions, gave the macrocyclic azulenophanes **10** as a blue solid, and **11** as a blue/green solid, in 6% and 2% yields, respectively.

When the oxidative coupling of the dilithium salt **8** was carried out at 0°C, the *syn*-[2.2](1,6)azulenophane (**9**) was obtained as dark green needles in 17% yield, together with **10** (3%) and **11** (1.5%).

Synthesis of syn-[2.2](4,6)Azulenophane (**12**): For the synthesis of the azulenophane **12** (Scheme 3), 1,2-bis(azulen-6-yl)ethane (**3**)[13] proved to be a suitable starting material. Nucleophilic addition of **3** with methyllithium in refluxing diethyl ether, subsequent hydrolysis of the addition product with methanol at −70°C, and dehydrogenation of the bis(dihydroazulene) with *p*-chloranil in benzene at room temp. afforded 1,2-bis(4-methylazulen-6-yl)ethane (**14**) as blue prisms in 34% yield. Deprotonation of **14** with two equivalents of LDA in THF at room temp. gave a dark red solution of the dianion of **14**, whose reaction with tosyl chloride in THF at 0°C under high-dilution conditions yielded seven products which could be separated by chromatography. In addition to 1% of 1,2-bis(4-methylazulen-6-yl)ethene (**15**) and 8% of the starting material **14**, 7% of the expected azulenophane **12** could be isolated as blue needles. In addition to these products and the 4-chloromethyldiazulenylethanes **17** (6%) and **18** (2%), the violet crystalline oligoazulene **16** (3%) was formed, as well as the desired macrocyclic azulenophane **13** (0.2%) (blue solid).

When the coupling of the dianion of **14** was carried out at −40°C using tosyl bromide, the azulenophanes **12** and **13** were obtained in 10% and 1% yields, respectively, along with **15** (3%), **16** (2%) and **14** (15%).

Mechanistic Discussion of the Coupling Reaction: Unexpectedly, the coupling reaction of **8** yields the macrocyclic azulenophanes **10** and **11** at low temperature, while the *syn*-[2.2](1,6)azulenophane (**9**) can be obtained only at higher temperatures. An inspection of the stereochemistry of the intermediate diradical **19** may provide a reasonable explanation for this result (Scheme 4). Among the conformers resulting from rotation around the C−C single bond in the ethano bridge, the *anti* conformer *s-trans*-**19** should be the more stable conformation, while the *syn* conformer *s-cis*-**19** should be less stable, due to static repulsion between the two radical centers. The intermolecular coupling reactions of both *s-trans*-**19** and *s-cis*-**19** should lead to the formation of the macrocyclic azulenophanes **10** and **11**, while **9** can only result from an intramolecular coupling reaction of *s-cis*-**19**. The energy barrier for the transformation of the energetically more favored *s-trans*-**19** into the less stable *s-cis*-**19** may be responsible for the higher reaction temperature required for the formation of **9**.

The formation of **15** suggests a partial deprotonation of the ethano bridge of **14** to give the dilithium salt **20**, and results from the reaction of **20** with tosyl halide (Scheme 5). The azulenophanes **12** and **13** could be formed via the dilithium salt **21** by a radical coupling reaction or a nucleophilic displacement reaction (Scheme 5). The deprotonation of **14** should mainly yield dilithium salt **21**, which may react with tosyl halide to give the diradical **23**, or the monolithium salt **22**. The intramolecular coupling reaction of the diradical **23** should yield the azulenophane **12**, while the intermolecular coupling reaction of **23** results in **13**. Alternatively, the intramolecular and intermolecular nucleophilic displacement reactions of the monolithium salt **22** can also yield the azulenophanes **12** and **13**, respectively. The formation of compounds **17** and **18** provides evidence
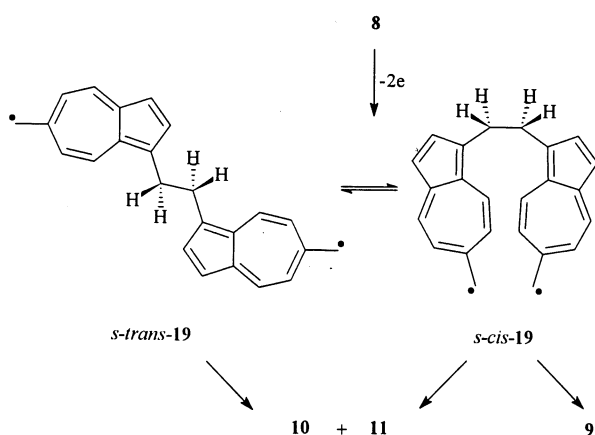
Scheme 2
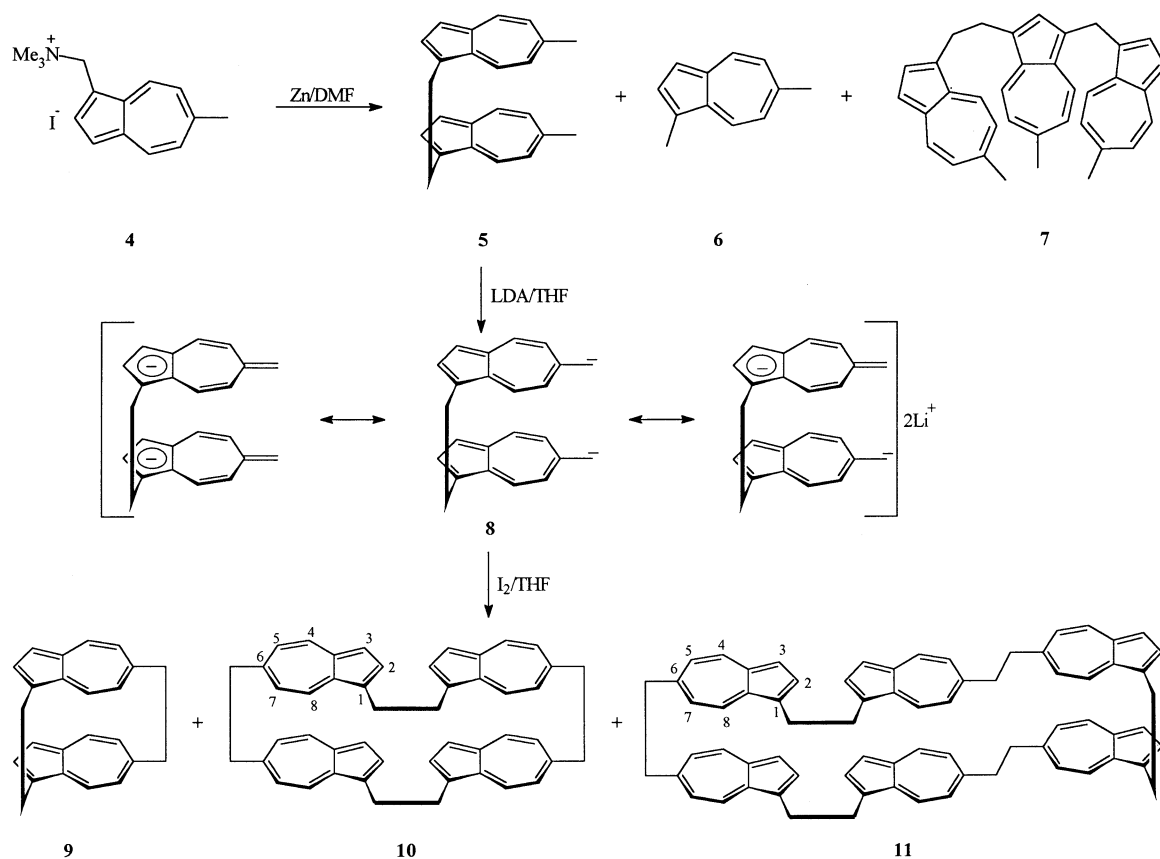
Scheme 3
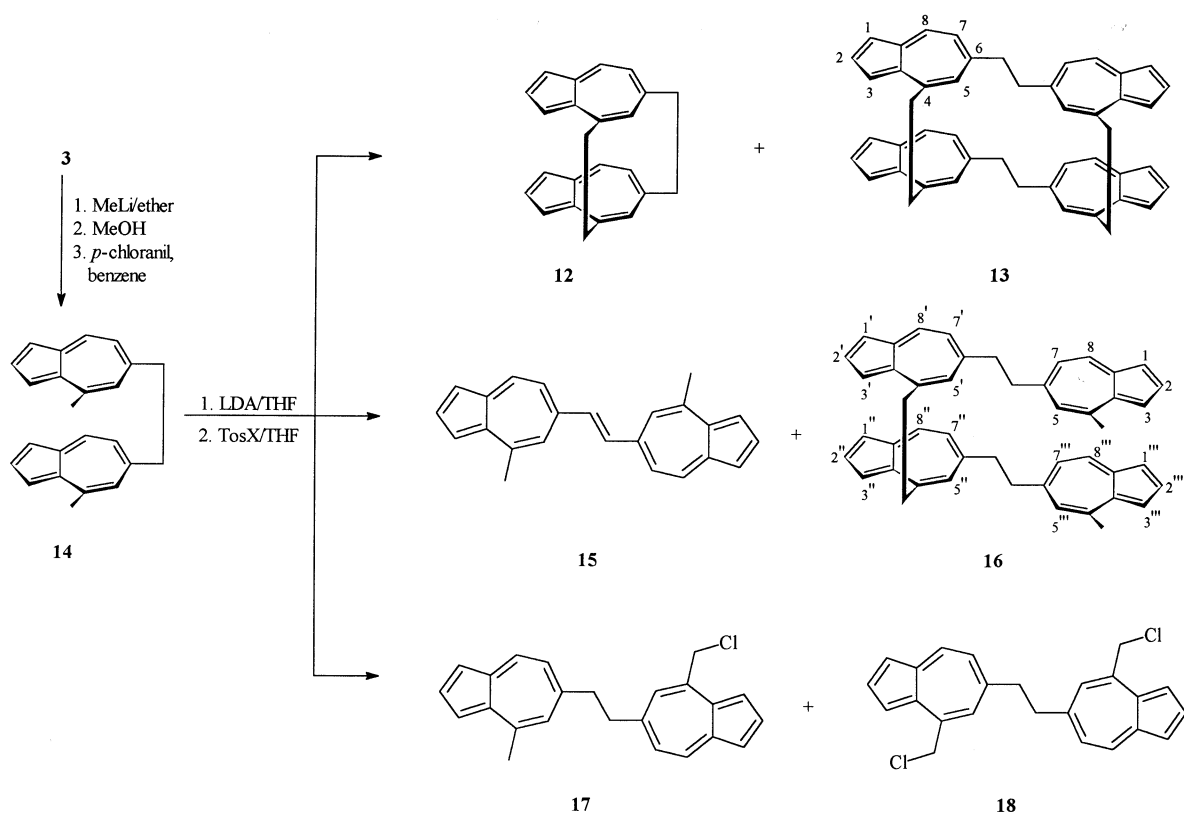
Scheme 4

for the existence of intermediate **22**. A hydrogen abstraction or hydrolysis of the corresponding reactive intermediates yields the starting material **14** and the oligoazulene **16**, respectively.

Conformational Behaviour of the Azulenophanes 9−13

There are two conformers for both **9** and **12** (Figure 1), of which **9A** and **12A** consist of a "stepwise structure" for the aromatic planes. The conformers **9B** and **12B** feature a face stacking of the aromatic planes. Both of the confor-

mational isomers of **9** or **12** should give rise to two distinct AA′BB′ spin systems for the two bridging ethano groups. In agreement with this expectation, each of the 300-MHz ¹H-NMR spectra of **9** and **12** clearly shows two distinct AA′BB′ spin systems in the upfield region, establishing that compound **9** obtained in the reaction is one of the conformational isomers (**9A** or **9B**), and **12** is one of the isomers (**12A** or **12B**).

A distinction between the two conformations of the azulenophanes **9** and **12** is possible, assuming interdeck magnetic anisotropy effects. The conformer **9A** should display large upfield shifts for the pair of two proton sets (7-H, 8-H) close to the inversion center, and small changes in chemical shifts for the remaining aromatic signals, compared with those of 1,6-dimethylazulene (**6**). The conformer **12A** is expected to display a large upfield shift for the inner aromatic proton (5-H), and downfield shifts for the remaining outer aromatic protons, compared with the corresponding proton signals of 4,6-dimethylazulene[15]. Both of the conformers **9B** and **12B** would be expected to show moderate upfield shifts for all the aromatic protons in comparison with the aromatic proton signals of the corresponding reference compounds, as in the case of *syn-* and *anti-*[2.2](2,6)azulenophanes[1][3][4][5].

The large upfield shifts ($\Delta\delta = 1.90$ for the azulenic proton 7-H, 1.84 for 8-H) and small changes in the remaining azulenic proton resonance (within a margin of 0.3 ppm) in
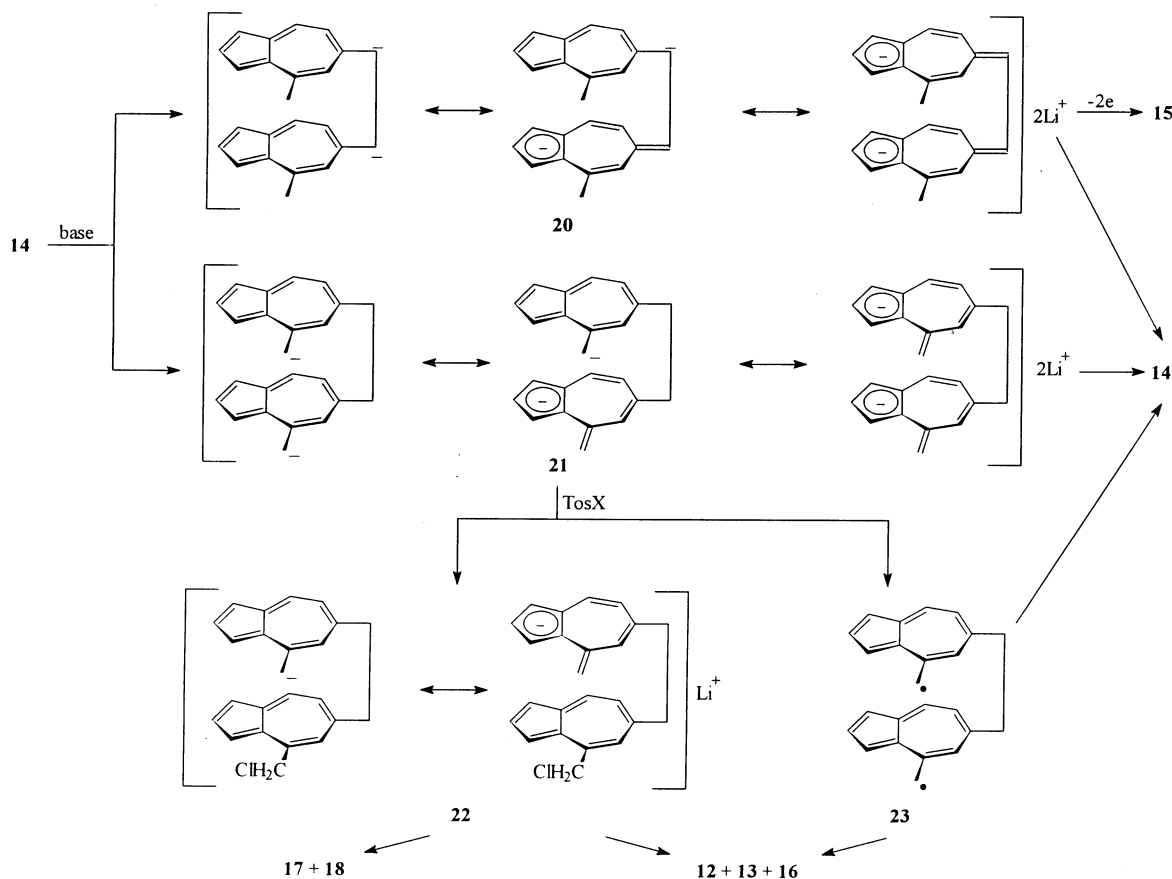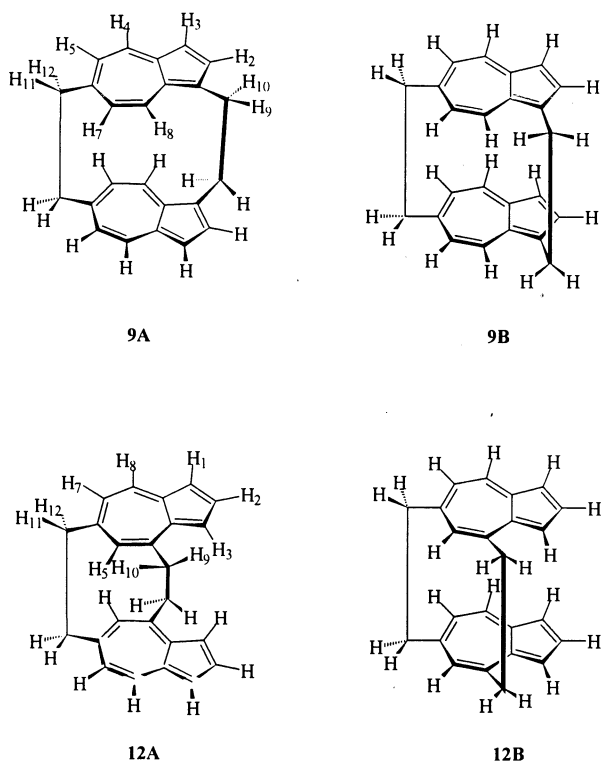
Scheme 5

Figure 1. Conformations of the azulenophanes **9** and **12**

9A **9B**

12A **12B**

the ^{1}H-NMR spectrum of **9**, in comparison with the azulenic proton signals of 1,6-dimethylazulene, support the formation of the conformational isomer **9A**. The large upfield shift ($\Delta\delta$ = 1.46) for the inner aromatic protons (5-H) and downfield shifts of outer aromatic protons ($\Delta\delta$ = 0.19 for 3-H, 0.06 for 2-H, 0.08 for 1-H, 0.12 for 8-H, 0.04 for 7-H) in the ^{1}H-NMR spectrum of **12**, compared with the aromatic proton signals of 4,6-dimethylazulene, suggest the formation of the conformational isomer **12A**.

The assignment of the individual aliphatic proton resonances of **9A** and **12A** can be made with the aid of their 2D-NOESY ^{1}H-NMR spectra. The NOESY spectrum of **9A** shows that 9-H (δ = 2.95) correlates with 8-H, 10-H (δ = 3.40) with 2-H, 11-H (δ = 2.48) with 7-H, and 12-H (δ = 3.09) with 5-H. The NOESY spectrum of **12A** indicates that 9-H (δ = 4.25) correlates with 3-H and 10-H, 10-H (δ = 2.53) with 5-H, 11-H (δ = 2.34) with 5-H and 12-H, 12-H (δ = 3.35) with 7-H. Temperature-dependent ^{1}H-NMR spectra of **9A** in Cl$_2$CD–CDCl$_2$ show that the chemical shifts of the protons, particularly the AA′BB′ patterns of the bridged ethano groups, are almost unchanged up to 130°C, indicating that **9A** is conformationally rigid up to this temperature. Temperature-dependent ^{1}H-NMR spectra of **12A** in Cl$_2$CD–CDCl$_2$ indicate that the aliphatic proton signals are slightly broadened up to 130°C, while the aromatic proton signals, especially the downfield shifted proton signals, are almost unchanged. Therefore, the broadening of the aliphatic proton signals of **12A** at 130°C is not due to a conformational flipping, but due to a flipping of the azulene rings.

The ^{1}H-NMR spectra of the macrocyclic azulenophanes **10**, **11** and **13** at room temperature clearly show two sharp singlets for two different ethano bridges, which suggests the presence of a rapid dynamic process, e.g. flipping of the azulene rings in these phanes. All aromatic proton signals of both **10** and **11** exhibit upfield shifts when compared with those of **6**, indicating the presence of a considerable shielding effect, decreasing in magnitude with an increase in the macrocyclic ring size. These observations suggest that the azulene rings in **10** and **11** predominantly adopt the "face-to-face" conformation where the aromatic protons are shielded by other azulene rings, and the magnitude of the shielding effect diminishes with an increase in the transannular distance of the macrocyclic azulenophanes. The aromatic proton signals of **13** show one upfield shift ($\Delta\delta$ = 0.13) for the inner protons (5-H), and downfield shifts for the outer protons ($\Delta\delta$ = 0.24 for 3-H, $\Delta\delta$ = 0.10 for 2-H, $\Delta\delta$ = 0.05 for 1-H, $\Delta\delta$ = 0.04 for 8-H, and $\Delta\delta$ = 0.01 for 7-H), when compared with those of 4,6-dimethylazulene. These observations suggest that the azulene rings in **13** are predominantly in the "head-to-head" conformation.

Attempts to investigate the conformation of **10** using low-temperature ^{1}H-NMR techniques failed, as the chemical shifts of the proton signals, particularly two singlets due to two different ethano bridges in **10**, remained almost unchanged in CD$_2$Cl$_2$ even at −90°C. Measurements below −90°C were impossible due to the poor solubility of **10** in organic solvents.

Electronic Spectra of the Azulenophanes 9–13

The visible part of the electronic spectrum of **9A** in *n*-hexane shows some slightly broadened absorptions with a maximum at 618 nm, which is shifted bathochromically by 22 nm in comparison with that of **6**[14]. These features, broadening of the bands and a considerable bathochromic shift of the absorption maximum for the first absorption band, are commonly observed for [2.2]cyclophanes. The similarities between the physical properties of *syn*- and *anti*-[2.2](2,6)azulenophanes[1][3][4][5] are also expected for *syn*- and *anti*-[2.2](1,6)azulenophanes. However, it is surprising that although compound **9A** and its *anti* isomer[6] obviously have the same conformation, their electronic spectra are different: two new bands between 462 and 495 nm are observed in the electronic spectrum of *anti*-[2.2](1,6)azulenophane when compared to that of **6**, and may be due to a transannular interaction between two facing rings[6], but no such additional bands are observed in the visible region of the electronic spectrum of **9A**. The difference between the electronic spectra of *syn*- and *anti*-[2.2](1,6)azulenophanes may result from different dipole orientations of the azulene units in the two isomers.

The visible part of the electronic spectrum of **12A** in 1,4-dioxane shows broadened absorptions with a maximum at 565 nm, shifted bathochromically by 13 nm in comparison with that of 4,6-dimethylazulene[15], while no additional band due to the transannular charge-transfer interaction between two azulene rings in **12A** is observed. The small bathochromic shift of the absorption maximum and the loss

of a clear transannular charge-transfer band in the visible region of the electronic spectrum of **12A**, compared to that of 4,6-dimethylazulene, may result from the partial overlap of the two azulene decks due to the "stepwise structure" of **12A**.

The electronic spectra of **10**, **11** and **13** are very similar to those of the corresponding reference compounds 1,6-dimethylazulene (**6**)[14] and 4,6-dimethylazulene[15], respectively, implying that the azulene rings of these macrocyclic phanes have a "normal" geometry (i. e. not considerably distorted).

Protonation of the Azulenophanes 9A and 12A

The protonation of **9A** and **12A** was studied by UV/Vis spectroscopy (Scheme 6). Solutions of **9A** and **12A** were prepared in dichloromethane containing various concentrations of proton acids, and their spectra were recorded.

Scheme 6
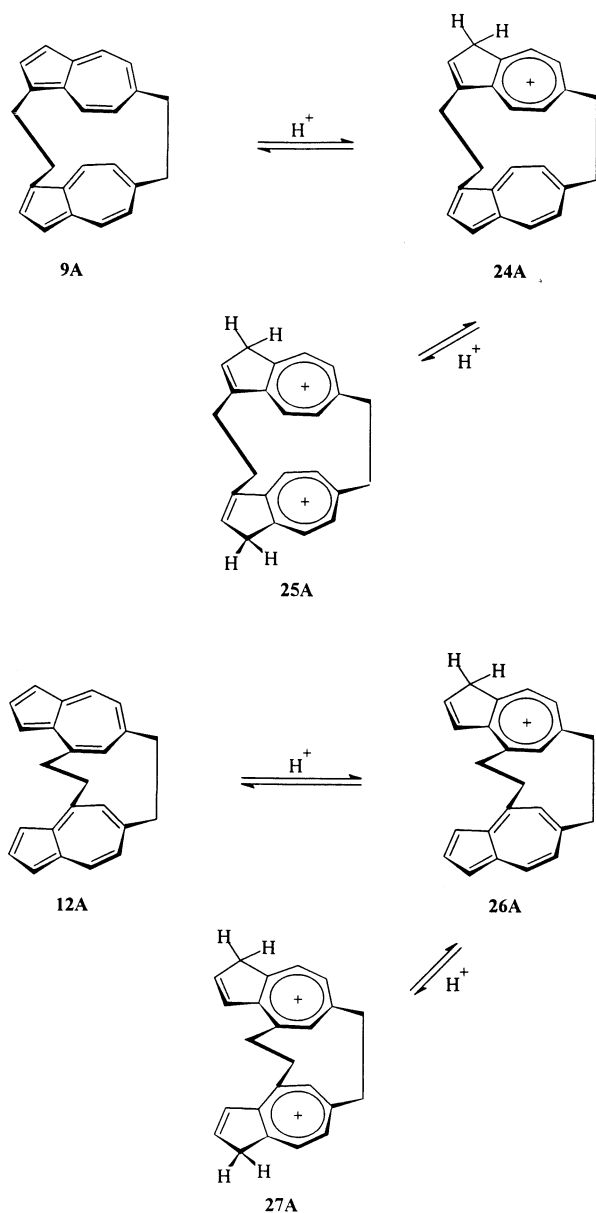
The spectral data of **9A** in dichloromethane, containing various acid concentrations, are listed in Table 1. At low acid concentrations (0−10% TFA in CH_2Cl_2) there is an increase in optical density of the long wavelength absorption, as well as a strong bathochromic shift of this band from 621 to 722 nm. Furthermore, a new absorption at 417 nm appears, which reaches a maximum at an acid concentration of 10% TFA. In addition, there is an increase in optical density at 368 nm, and a decrease at 278 nm. The spectrum of **9A** in 10% TFA can be assigned to that of the monoprotonated azulenophane **24A**, and the absorption at 417 nm indicates the existence of charge-transfer interaction between the azulene donor and the tropylium-like acceptor. A similar charge-transfer band was also observed in the monoprotonated *syn*- and *anti*-[2.2](2,6)azulenophanes[1][3].

When the acid concentration is increased (Table 1), even the second azulene deck will be protonated as shown by the changes in the spectra. The bands at 284 and 722 nm as well as the charge-transfer absorption at 417 nm disappear, while the band at about 370 nm, characteristic for the two azulenium ions[1][3] in the double protonated azulenophane **25A**, increases.

Table 1. UV/Vis spectra of **9A** in proton acids

Acid medium	λ_{max} [nm] (lg ε)			
CH_2Cl_2	278 (4.88)	352 (3.72)		621 (2.84)
1% TFA in CH_2Cl_2	275 (4.52)	368 (3.96)	417 (3.41)	658 (3.39)
2% TFA in CH_2Cl_2	273 (4.50)	366 (3.97)	417 (3.53)	667 (3.59)
5% TFA in CH_2Cl_2	284 (4.37)	368 (4.10)	417 (3.84)	718 (4.66)
10% TFA in CH_2Cl_2	284 (4.33)	368 (4.11)	417 (3.87)	722 (4.75)
50% TFA in CH_2Cl_2	271 (4.39)	368 (4.16)		678 (4.17)
100% TFA		368 (4.39)		663 (3.23)
30% H_2SO_4		371 (4.51)		

Table 2 lists the spectral data of **12A** in dichloromethane with various concentrations of TFA. At low acid concentrations (0−2.5% TFA in dichloromethane) there is a general increase in optical density of the long-wavelength absorption, and a small bathochromic shift of this band from 562 to 577 nm. In addition, there is an increase in optical density of the absorption at about 360 nm. The spectrum of **12A** in 1−2.5% TFA is assigned to that of the monoprotonated azulenophane **26A**. In contrast to **24A**, no new band due to an intramolecular transannular charge-transfer interaction was observed in the spectrum of **26A**, which again indicates the insufficient overlap between the protonated and unprotonated azulene decks in **26A** due to its "stepwise structure".

As the acid concentration is increased (Table 2), a twofold protonation begins to occur, and again this is shown

by the changes in the spectra. The absorption at 577 nm almost disappears, and the band at about 360 nm, characteristic for the two azulenium ions[1][3] in the twofold protonated azulenophane **27A**, increases.

Table 2. UV/Vis spectra of the azulenophane **12A** in dichloromethane containing various concentrations of TFA

Conc. of TFA (%)	λ_{max} [nm] (lg ε)	
0	348 (4.06)	562 (3.02)
1	359 (4.27)	575 (3.41)
2	359 (4.30)	577 (3.39)
2.5	360 (4.30)	577 (3.38)
5	362 (4.33)	577 (3.25)
10	365 (4.36)	579 (2.97)
40	366 (4.43)	560 (1.97)
100	364 (4.37)	565 (1.87)

Scheme 7

28A   **29A**

POCl₃/DMF

9A

H₂CO/AcOH
Me₂NCH₂NMe₂

30A   **31A**
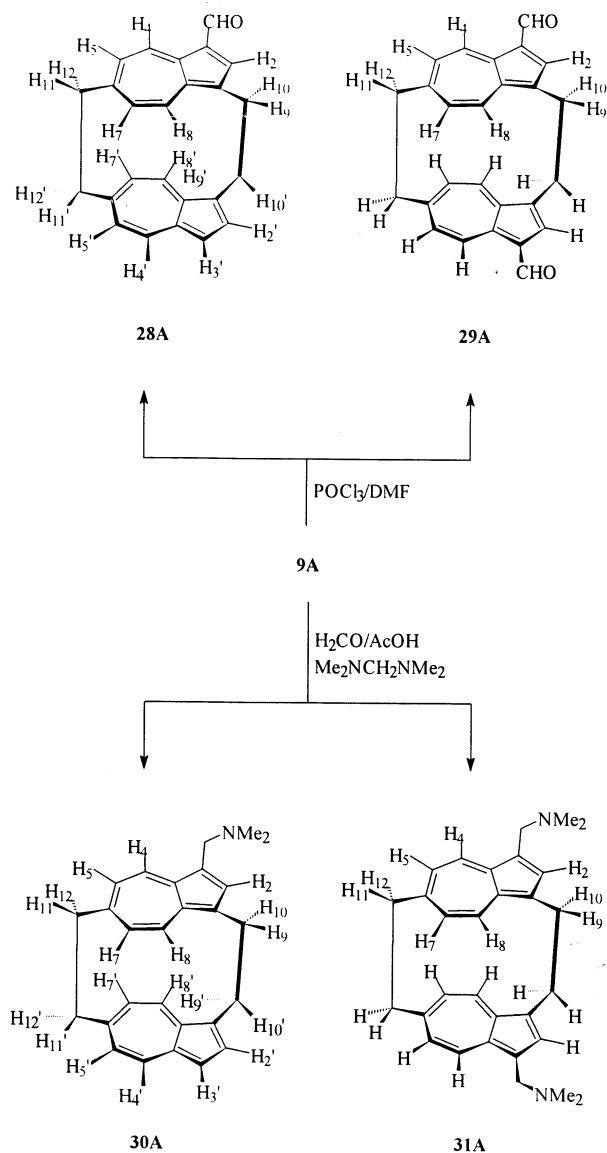
Formylation and Aminomethylation of *syn*-[2.2](1,6)Azulenophane (9A)

In order to examine the reactivity of the new azulenophanes in comparison to azulenes, the Vilsmeier formylation and aminomethylation of **9A** were performed (Scheme 7)[16]. Reaction of **9A** with 1.5 mol equivalents of phosphoryl chloride in DMF at room temperature led to 3-formyl-*syn*-[2.2](1,6)azulenophane (**28A**) in 15% yield. Under the same reaction conditions a twofold formylation of **9A** with 3 mol-equivalents of phosphoryl chloride afforded 3,3′-diformyl-*syn*-[2.2](1,6)azulenophane (**29A**) in 42% yield. Aminomethylation of **9A** with paraformaldehyde and *N,N,N′,N′*-tetramethyldiaminomethane in the presence of acetic acid furnished the Mannich bases 3-*N,N*-dimethylaminomethyl-*syn*-[2.2](1,6)azulenophane (**30A**) and 3,3′-bis(*N,N*-dimethylaminomethyl)-*syn*-[2.2](1,6)azulenophane (**31A**) in 40% and 46% yields, respectively. It would be expected that a substituent at the 3-position of the azulenophane **9A** could change the reactivity of the second deck by an intramolecular transannular interaction. However, the twofold formylation and aminomethylation of **9A** occured under the same reaction conditions as used for the monoformylation and monoaminomethylation of **9A**. Furthermore, the ¹H-NMR spectra of **28A** and **30A** show that the aromatic proton resonance signals in the unsubstituted azulene unit are almost identical with the corresponding aromatic proton signals of **9A**. These results imply that the functional group in **28A** or **30A** does not affect the π-electron system of the second deck. The ¹H-NMR spectra of the phanes **28A**−**30A** show large upfield shifts for the signals due to the protons at the 7- and 8-positions, which indicates that the conformation of **9A** is not changed under the reaction conditions.

Experimental Section

NMR: Bruker WM 300, AC 300, ARX 300 (¹H: 300 MHz, ¹³C: 75.47 MHz), and Varian XL-100 (¹H: 100 MHz). ¹H- and ¹³C-NMR spectra were measured with TMS as internal standard. − MS: Finnigan MAT 311-A/100 MS. − IR: Beckman IR 5A, Perkin-Elmer 125. − UV/Vis: Beckman DK-2A, UV 5240. − Melting points: Kofler apparatus (Reichert, Vienna, Austria), uncorrected values. − Elemental analyses: Perkin-Elmer CHN 240 B. − Column chromatography: Basic alumina [activity B II−III (Brockmann) ICN Biomedicals] and silica gel [70−230 mesh (ASTM) Macherey-Nagel]. − All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under nitrogen in flame-dried glassware. Solvents were dried and distilled according to standard procedures.

1,2-Bis(azulen-6-yl)ethane (*3*)[13]: A 1.5 M solution of *n*-butyllithium (6.67 ml, 10 mmol) in *n*-hexane was added dropwise at −30 °C to a solution of diisopropylamine (1.0 g, 10 mmol) in THF (20 ml). The mixture was allowed to warm up to room temp. and stirred at this temp. for 1 h. A blue solution of 6-methylazulene (**1**) (1.42 g, 10 mmol) in THF (30 ml) was then added dropwise at −60 °C. The reaction mixture was stirred at −60 °C for 20 min to give a dark

brown solution of the lithium 6-azulenemethide (**2**). The solution was cooled to −100°C and a solution of iodine (1.26 g, 5 mmol) in THF (20 ml) was slowly added. The reaction solution turned blue again and was slowly warmed up to room temp. (over about 2 h) and water (75 ml) was added. After filtration, the filter cake was washed with water, then with methanol, and finally with diethyl ether to give 1.21 g (86%) of **3** as fine blue crystals, m.p. 320°C (dec.). − ^{1}H NMR (100 MHz, CDCl$_3$): δ = 3.22 (s, 4 H, 9-, 9′-H), 7.06 (d, J = 10.4 Hz, 4 H, 5-, 5′-, 7-, 7′-H), 7.35 (d, J = 3.7 Hz, 4 H, 1-, 1′-, 3-, 3′-H), 7.84 (t, J = 3.7 Hz, 2 H, 2-, 2′-H), 8.23 (d, J = 10.4 Hz, 4 H, 4-, 4′-, 8-, 8′-H). − IR (KBr): ṽ = 1601 cm^{-1}, 1575, 1390, 1195, 1045, 970, 835, 745. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 238 nm, 265 (sh), 275 (sh), 285 (sh), 290 (sh), 295, 318 (sh), 324, 331, 338, 346, 357 (sh), 418, 437 (sh), 567, 611, 673. − MS (70 eV); m/z (%): 282 (42) [M$^+$], 141 (100) [M$^+$ − C$_{11}$H$_9$]. − C$_{22}$H$_{18}$ (282.4): calcd. C 93.57, H 6.43; found C 92.79, H 6.13.

1-N,N,N-Trimethylammoniummethyl-6-methylazulene Iodide (**4**)[5]: A mixture of paraformaldehyde (1.2 g) and acetic acid (4 ml) was refluxed for 1h, then cooled to room temp. and a solution of 6-methylazulene (5.0 g, 35 mmol) and N,N,N',N'-tetramethyldiaminomethane (1.8 g, 17.6 mmol) in benzene/ethanol (3:2) (100 ml) was added. The reaction solution was stirred at 40°C for 4 h. The cooled mixture was diluted with diethyl ether (200 ml) and extracted twice with 2 N acetic acid (250 ml). The combined aqueous phases were made weakly alkaline with 2 N NaOH with cooling (ice bath) and extracted four times with diethyl ether (100 ml). The combined organic phases were washed with water, dried with sodium sulfate, and concentrated in vacuo. Chromatography of the residue on alumina with diethyl ether yielded 4.6 g (66%) of 1-N,N-dimethylaminomethyl-6-methylazulene as a blue oil. The oil was dissolved in diethyl ether (100 ml) and iodomethane (3.5 g, 25 mmol) was added with cooling (ice bath). The reaction mixture was stirred at 5°C for 16 h and a blue violet solid precipitated. The solid was filtered off, washed twice with diethyl ether (50 ml), and dried in vacuum to yield 7.5 g (63%, based on 6-methylazulene) of the ammonium salt **4** as a blue violet powder, m.p. 130°C (dec.). − ^{1}H NMR (100 MHz, [D$_6$]DMSO): δ = 2.69 (s, 3 H, −CH_3), 3.03 (s, 9 H, −N$^+$Me$_3$), 4.99 (s, 2 H, −CH_2N$^+$Me$_3$), 7.30−7.50 (m, 3 H, 3-, 5-, 7-H), 7.94 (d, J = 4 Hz, 1 H, 2-H), 8.44 (d, J = 10 Hz, 1 H, 4-H), 8.70 (d, J = 10 Hz, 1 H, 8-H). − IR (KBr): ṽ = 2990 cm^{-1} (C−H), 2930 (C−H), 1580 (C=C). − UV/Vis (methanol): λ$_{max}$ (lg ε) = 267 nm (4.28) (sh), 272 (4.48) (sh), 277 (4.62) (sh), 281 (4.76), 287 (4.73), 293 (4.75), 319 (3.77), 342 (3.75) (sh), 345 (3.80), 356 (3.38), 368 (2.94), 541 (2.63), 573 (2.59) (sh), 630 (2.25) (sh). − MS (FD, 10 mA); m/z (%): 214 (100) [M$^+$ − I]. − C$_{15}$H$_{20}$IN (341.2): calcd. C 52.79, H 5.91, N 4.10; found C 53.24, H 5.78, N 3.96.

Reductive Coupling Reaction of the Ammonium Salt **4**: According to ref.[11], zinc powder (18.0 g, 275 mmol) was added at room temp. to a solution of **4** (19.0 g, 55 mmol) in DMF (300 ml). The mixture was stirred for 26 h at 50°C and then cooled to room temp. The precipitate was filtered off and the filtrate was concentrated in vacuo. The residue was dissolved in diethyl ether (400 ml) and the solution was washed twice with 2 N acetic acid (100 ml), twice with water (200 ml), dried with magnesium sulfate, and concentrated in vacuo. Chromatography of the residue on alumina with n-hexane/dichloromethane (from 100:0 to 5:1) yielded **5**, **6** and **7**.

5: Yield 3.65 g (43%) as blue prisms, m.p. 152−153°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.61 (s, 6 H, 6-, 6′-CH_3), 3.46 (s, 4 H, Az−CH_2CH_2−Az′), 6.96 (br. d, J = 10 Hz, 4 H, 5-, 5′-, 7-, 7′-H), 7.25 (d, J = 3.7 Hz, 2 H, 3-, 3′-H), 7.68 (d, J = 3.7 Hz, 2 H, 2-, 2′-H), 8.10 (br. d, J = 10 Hz, 4 H, 4-, 4′-, 8-, 8′-H). − IR

(KBr): ṽ = 2890 cm^{-1} (C−H), 1602, 1580, 1390, 990, 955, 810, 774. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 237 nm (4.48), 283 (4.96), 290 (4.95), 296 (4.98), 328 (3.78) (sh), 341 (3.91) (sh), 352 (4.04), 367 (3.68), 589 (2.82), 636 (2.74) (sh), 700 (2.30) (sh). − MS (70 eV); m/z (%): 310 (100) [M$^+$]. − C$_{24}$H$_{22}$ (310.4): calcd. C 92.85, H 7.14; found C 92.59, H 7.22.

6: Yield 1.30 g (15%) as a blue oil. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.72 (s, 3 H, 6-CH_3), 2.81 (s, 3 H, 1-CH_3), 7.07 (br. d, J = 10 Hz, 2 H, 5-, 7-H), 7.40 (d, J = 3.7 Hz, 1 H, 3-H), 7.80 (d, J = 3.7 Hz, 1 H, 2-H), 8.21 (br. d, J = 10 Hz, 2 H, 4-, 8-H). − The UV/Vis data in n-hexane agreed with those reported in ref.[14]; UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 237 nm (4.19), 267 (4.30) (sh), 272 (4.49) (sh), 278 (4.66) (sh), 282 (4.77), 288 (4.75), 293 (4.71), 301 (4.97) (sh), 319 (3.23) (sh), 327 (3.35) (sh), 336 (3.52), 351 (3.67), 367 (3.18), 550 (2.38) (sh), 575 (2.47) (sh), 590 (2.50), 612 (2.46) (sh), 640 (2.42) (sh), 707 (1.97) (sh).

7: Yield 0.66 g (8%) as blue plates, m.p. 96°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.55, 2.57, 2.60 (3 s, each 3 H, 6-, 6′-, 6″-CH_3), 3.36 (s, 4 H, Az−CH_2CH_2−Az′−), 4.76 (s, 2 H, Az″−CH_2−Az′−), 6.83−6.99 (m, 6 H, 5-, 5′-, 5″-, 7-, 7′-, 7″-H), 7.20 (d, J = 3.7 Hz, 1 H, 3″-H), 7.39 (s, 1 H, 2′-H), 7.46 (d, J = 3.7 Hz, 1 H, 2-H), 7.62 (d, J = 3.7 Hz, 1 H, 2″-H), 7.99−8.25 (m, 6 H, 4-, 4′-, 4″-, 8-, 8′-, 8″-H). − IR (KBr): ṽ = 2805 cm^{-1} (C−H), 1608, 1590, 1395, 1290, 1215, 995, 806. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 243 nm, 285, 291, 296, 342 (sh), 352, 366 (sh), 478 (sh), 571 (sh), 599, 610, 641, 702 (sh), 749 (sh). − MS (70 eV); m/z (%): 464 (10) [M$^+$], 309 (100) [M$^+$ − C$_{12}$H$_{11}$], 279 (16), 155 (46) [C$_{12}$H$_{11}^+$]. − An analytically pure sample could not be obtained.

syn-[2.2](1,6)Azulenophane (**9**), *[2.2.2.2](1,6)Azulenophane* (**10**), *and [2.2.2.2.2.2]-(1,6)Azulenophane* (**11**): A 1.5 M solution of n-butyllithium (6.67 ml, 10 mmol) in n-hexane was added dropwise at −30°C to a solution of diisopropylamine (1.2 g, 12 mmol) in THF (20 ml). The mixture was allowed to warm up to room temp. and stirred at this temperature for 1 h. Then a solution of **5** (1.24 g, 4 mmol) in THF (33 ml) was added dropwise at room temp. The reaction mixture was stirred at room temp. for 30 min to give a brown red solution of the dilithium salt **8**. The solution of **8** (about 60 ml) and a solution of iodine (1.26 g, 5 mmol) in THF (60 ml) were simultaneously added dropwise to vigorously stirred THF (250 ml), (a) at −80°C; (b) at 0°C, within 18 h using a two-syringe infusion pump. After the addition, the reaction mixture was allowed to warm up to room temp. and stirred at this temperature for 6 h. After the addition of methanol (50 ml) the insoluble solid was filtered off and the filtrate was concentrated in vacuo. The residue was extracted with chloroform (200 ml). The solution was washed twice with water (100 ml), dried with magnesium sulfate, and concentrated in vacuo. Chromatography of the residue was carried out on silica gel with n-hexane/dichloromethane (from 10:1 to 1:1). (a) Yield 113 mg (9%) of **5**, 68 mg (6%) of **10**, and 23 mg (2%) of **11**; (b) Yield 35 mg (3%) of **5**, 209 mg (17%) of **9**, 39 mg (3%) of **10**, and 17 mg (1.5%) of **11**.

9: Dark green needles, m.p. 180°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.48 (m, AA′BB′, 2 H, 11-H), 2.95 (m, AA′BB′, 2 H, 9-H), 3.09 (m, AA′BB′, 2 H, 12-H), 3.40 (m, AA′BB′, 2 H, 10-H), 5.17 (dd, J_1 = 10.3 Hz, J_2 = 1.5 Hz, 2 H, 7-H), 6.37 (d, J = 10.3 Hz, 2 H, 8-H), 6.77 (dd, J_1 = 9.5 Hz, J_2 = 1.5 Hz, 2 H, 5-H), 7.21 (d, J = 3.8 Hz, 2 H, 3-H), 7.71 (d, J = 3.8 Hz, 2 H, 2-H), 8.03 (d, J = 9.5 Hz, 2 H, 4-H). − ^{13}C NMR (CDCl$_3$): δ = 152.04, 142.24, 135.97, 135.54, 134.52, 133.82, 133.72, 124.42, 122.17, 115.67, 44.54, 31.74. − IR (KBr): ṽ = 2900 cm^{-1}, 2850 (C−H), 1575, 1500, 1430, 1380, 1320, 1290, 1250, 1210, 1175, 1005, 955, 915, 900, 885, 865, 825, 810, 760, 705, 645. − UV/Vis (n-hexane): λ$_{max}$ (lg ε) =

247 nm (4.47) (sh), 275 (4.84), 297 (4.42) (sh), 339 (3.67) (sh), 352 (3.67), 395 (3.11) (sh), 572 (2.66) (sh), 595 (2.74) (sh), 618 (2.81), 642 (2.79), 675 (2.79), 707 (2.58) (sh), 748 (2.41). − MS (70 eV); *m/z* (%): 308 (18) [M$^+$], 154 (100) [1/2 M$^+$]. − C$_{24}$H$_{20}$ (308.4): calcd. C 93.46, H 6.54; found C 93.64, H 6.50.

10: Blue solid, m.p. 265°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.11 (s, 8 H, −C*H$_2$*C*H$_2$*−), 3.25 (s, 8 H, −C*H$_2$*C*H$_2$*−), 6.22 (dd, J_1 = 10.0 Hz, J_2 = 1.3 Hz, 4 H, 7-H), 6.93 (dd, J_1 = 10.0 Hz, J_2 = 1.3 Hz, 4 H, 5-H), 7.15 (d, J = 3.7 Hz, 4 H, 3-H), 7.58 (d, J = 3.7 Hz, 4 H, 2-H), 7.61 (d, J = 10.0 Hz, 4 H, 8-H), 8.09 (d, J = 10.0 Hz, 4 H, 4-H). − IR (KBr): ṽ = 2920 cm^{-1}, 2850 (C−H), 1580, 1570, 1560, 1500, 1460, 1445, 1430, 1400, 1380, 1300, 1260, 1185, 1080, 1015, 960, 930, 820, 800, 770, 710, 660. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 240 nm (4.76), 282 (5.24), 287 (5.22) (sh), 296 (5.10) (sh), 341 (4.19) (sh), 352 (4.25), 367 (3.84) (sh), 594 (3.10), 616 (3.06), 642 (3.03), 710 (2.59) (sh). − MS (70 eV); *m/z* (%): 616 (14) [M$^+$], 462 (8) [3/4 M$^+$], 460 (18), 308 (11) [1/2 M$^+$], 154 (100) [1/4 M$^+$]. − HRMS (C$_{48}$H$_{40}$): calcd. 616.3130; found 616.3155.

11: Blue green solid, m.p. 151°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.04 (s, 12 H, −C*H$_2$*C*H$_2$*−), 3.35 (s, 12 H, −C*H$_2$*C*H$_2$*−), 6.72 (dd, J_1 = 10.1 Hz, J_2 = 1.2 Hz, 6 H, 7-H), 6.87 (dd, J_1 = 9.8 Hz, J_2 = 1.1 Hz, 6 H, 5-H), 7.18 (d, J = 3.8 Hz, 6 H, 3-H), 7.65 (d, J = 3.8 Hz, 6 H, 2-H), 7.84 (d, J = 10.1 Hz, 6 H, 8-H), 8.04 (d, J = 9.8 Hz, 6 H, 4-H). − IR (KBr): ṽ = 2900 cm^{-1}, 2850 (C−H), 1602, 1565, 1500, 1430, 1390, 1300, 1250, 1235, 1200, 1088, 990, 960, 885, 826, 765, 706. UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 240 nm, 283 (sh), 292, 299, 338, 352, 367, 595, 616 (sh), 643, 713 (sh). − FDMS (0−20 mA); *m/z* (%): 924 (100) [M$^+$], 462 (8) [1/2 M$^+$]. − An analytically pure sample could not be obtained.

4,6-Dimethylazulene: According to ref.[15], a solution of 1.0 M methyllithium (51 ml, 51 mmol) in diethyl ether was added dropwise at room temp. to a solution of 6-methylazulene (**1**) (7.1 g, 50 mmol) in diethyl ether (30 ml). The mixture was refluxed for 4 h and a light yellow solid precipitated. After cooling the mixture to −70°C, methanol (10 ml) was added dropwise. The reaction solution was allowed to warm up to room temp. and *p*-chloranil (15.0 g, 50 mmol) and benzene (50 ml) were added. The mixture was stirred at room temp. for 17 h and then filtered through alumina with *n*-hexane as eluent. The violet eluent was washed with 2 N NaOH and water, dried with magnesium sulfate, and concentrated in vacuo. Chromatography of the residue on silica gel with *n*-hexane yielded 2.24g (29%) of 4,6-dimethylazulene as a violet oil. An analytically pure sample could not be obtained. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.63 (s, 3 H, 6-C*H$_3$*), 2.87 (s, 3 H, 4-C*H$_3$*), 7.02 (d, J = 9.7 Hz, 1 H, 7-H), 7.10 (s, 1 H, 5-H), 7.28 (dd, J_1 = 3.8 Hz, J_2 = 1.4 Hz, 1 H, 1-H), 7.34 (d, J = 3.8 Hz, 1 H, 3-H), 7.71 (t, J = 3.8 Hz, 1 H, 2-H), 8.19 (d, J = 9.7 Hz, 1 H, 8-H). − ^{13}C NMR (CDCl$_3$): δ = 24.89 (4-CH$_3$), 28.46 (6-CH$_3$), 115.76 (C-3), 118.70 (C-1), 123.19 (C-7), 128.06 (C-5), 133.83 (C-2), 136.02 (C-8), 136.29, 138.51, 145.75, 147.69.− UV/Vis (1,4-dioxane): λ$_{max}$ = 240 nm, 278 (sh), 282, 288, 302, 324 (sh), 331, 340 (sh), 346, 552, 568 (sh), 592, 649. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 240 nm, 278 (sh), 283, 288, 302 (sh), 324 (sh), 332, 340 (sh), 347, 550, 585 (sh), 642 (sh). − IR (film): ṽ = 2900 cm^{-1}, 2850, 1575, 1565, 1430, 1360, 1060, 1025, 824, 784, 743.

1,2-Bis(4-methylazulen-6-yl)ethane (**14**): A solution of methyllithium (1.0 M, 100 ml, 100 mmol) in diethyl ether was added dropwise at room temp to a suspension of 1,2-bis(azulen-6-yl)ethane (**3**) (10.0 g, 35 mmol) in diethyl ether (250 ml). The mixture was refluxed for 10 h and a pale yellow precipitate formed. After cooling the mixture to −70°C, methanol (20 ml) was added drop-

wise and the reaction mixture was allowed to warm up to room temp. Then 2 N HCl (200 ml) was added and the organic layer was separated, washed with water (250 ml), dried with magnesium sulfate, and concentrated in vacuo. To the solution of the residue in benzene (250 ml) *p*-chloranil (17.2 g, 70 mmol) was added portionwise at room temp. and the mixture was stirred at room temp. for 40 h, then washed with 2 N NaOH and water, dried with magnesium sulfate, and concentrated in vacuo. Chromatography of the residue on alumina with *n*-hexane/dichloromethane (5:1) yielded 3.79 g (34%) of **14** as violet blue prisms, m.p. 199−200°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.87 (s, 6 H, 4-, 4′-C*H$_3$*), 3.18 (s, 4 H, −C*H$_2$*C*H$_2$*−), 7.02 (dd, J_1 = 9.7 Hz, J_2 = 1.2 Hz, 2 H, 7-, 7′-H), 7.10 (s, 2 H, 5-, 5′-H), 7.32 (dd, J_1 = 3.8 Hz, J_2 = 1.4 Hz, 2 H, 1-, 1′-H), 7.37 (d, J = 3.8 Hz, 2 H, 3-, 3′-H), 7.76 (t, J = 3.8 Hz, 2 H, 2-, 2′-H), 8.23 (d, J = 9.7 Hz, 2 H, 8-, 8′-H). − ^{13}C NMR (CDCl$_3$): δ = 24.96 (4-, 4′-CH$_3$), 45.85 (−CH$_2$CH$_2$−), 115.90 (C-3, C-3′), 118.83 (C-1, C-1′), 122.94 (C-7, C-7′), 127.74 (C-5, C-5′), 134.35 (C-2, C-2′), 136.26 (C-8, C-8′), 136.47, 138.73, 146.10, 150.46. − UV/Vis (1,4-dioxane): λ$_{max}$ (lg ε) = 242 nm (4.62), 279 (4.78) (sh), 287 (4.94) (sh), 292 (5.01) (sh), 297 (5.09), 326 (3.96) (sh), 333 (4.04), 341 (4.03) (sh), 348 (4.16), 358 (3.44) (sh), 422 (2.12) (sh), 450 (2.22) (sh), 557 (2.91), 570 (2.88) (sh), 596 (2.84), 655 (2.39) (sh). − IR (KBr): ṽ = 2900 cm^{-1}, 2850, 1602, 1545, 1480, 1420, 1390, 1360, 1250, 1200, 1052, 1005, 934, 915, 865, 830, 790, 740, 706. − MS (70 eV); *m/z* (%): 310 (96) [M$^+$], 295 (5) [M$^+$ − Me], 280 (3) [M$^+$ − 2 Me], 155 (100) [1/2 M$^+$], 153 (44), 139 (15), 128 (25), 115 (25). − C$_{24}$H$_{22}$ (310.4): calcd. C 92.86, H 7.14; found C 92.81, H 7.34.

syn-[2.2](4,6)Azulenophane (**12**) and [2.2.2.2](4,6)Azulenophane (**13**): (a) A solution of *n*-butyllithium (1.5 M, 13.33 ml, 20 mmol) in *n*-hexane was added dropwise at 0°C to a solution of diisopropylamine (2.4 g, 24 mmol) in THF (20 ml). The mixture was allowed to warm up to room temp. and stirred at this temperature for 30 min. Then a solution of **14** (2.0 g, 6.4 mmol) in THF (167 ml) was added dropwise at room temp. The reaction mixture was stirred at room temp. for 30 min to give a dark red solution of the dilithium salts **20** and **21**. The solution of **20** and **21** (about 200 ml) and a solution of tosyl chloride (1.91 g, 10 mmol) in THF (200 ml) were simultaneously added dropwise to vigorously stirred THF (300 ml) at 0°C within 20 h by using a two-syringe infusion pump. After the addition the reaction mixture was allowed to warm to room temp. and stirred at this temperature for 5 h. Then methanol (30 ml) was added and the insoluble solid was filtered off. The filtrate was concentrated in vacuo and the residue was extracted with dichloromethane (500 ml). The solution was washed with 2 N NaOH (100ml), then with 2 N HCl (100 ml), and finally with water (100 ml), dried with magnesium sulfate, and concentrated in vacuo. Chromatography of the residue was carried out on silica gel with *n*-hexane/dichloromethane (from 4:1 to 3:2) to give seven fractions.

Fraction 1: Yield 21 mg (1%) of **15** as dark green needles, m.p. 190°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.97 (s, 6 H, 4-, 4′-C*H$_3$*), 7.34 (dd, J_1 = 3.8 Hz, J_2 = 1.4 Hz, 2 H, 1-, 1′-H), 7.39 (d, J = 3.8 Hz, 2 H, 3-, 3′-H), 7.43 (d, J = 9.9 Hz, 2 H, 7-, 7′-H), 7.46 (s, 2 H, 5-, 5′-H), 7.50 (s, 2 H, 9-, 9′-H), 7.79 (t, J = 3.8 Hz, 2 H, 2-, 2′-H), 8.33 (d, J = 9.9 Hz, 2 H, 8-, 8′-H). − UV/Vis (1,4-dioxane): λ$_{max}$ = 252 nm, 258, 272 (sh), 287 (sh), 298 (sh), 329, 343 (sh), 418, 437 (sh), 613. − IR (KBr): ṽ = 1602 cm^{-1}, 1535, 1470, 1390, 1360, 1260, 1230, 1054, 1005, 970, 952, 834, 790, 752. − MS (70 eV); *m/z* (%): 308 (100) [M$^+$], 293 (22) [M$^+$ − Me], 278 (28) [M$^+$ − 2 Me], 179 (84) [M$^+$ − C$_{11}$H$_9$], 165 (13), 154 (16), 152 (11), 139 (18), 115 (15). − An analytically pure sample could not be obtained.

Fraction 2: Yield 160 mg (8%) of **14**.

Fraction 3: Yield 144 mg (7%) of **12** as blue needles, m.p. 241 °C (dec.). − ¹H NMR (300 MHz, CDCl₃): δ = 2.34 (m, AA′BB′, 2 H, 11-H), 2.53 (m, AA′BB′, 2 H, 10-H), 3.35 (m, AA′BB′, 2 H, 12-H), 4.25 (m, AA′BB′, 2 H, 9-H), 5.64 (s, 2 H, 5-H), 7.06 (d, *J* = 9.9 Hz, 2 H, 7-H), 7.36 (dd, *J₁* = 3.7 Hz, *J₂* = 1.1 Hz, 2 H, 1-H), 7.53 (d, *J* = 3.4 Hz, 2 H, 3-H), 7.77 (t, *J* = 3.8 Hz, 2 H, 2-H), 8.31 (d, *J* = 9.5 Hz, 8-H). − ¹³C NMR (CDCl₃): δ = 40.19 (−CH₂CH₂−), 45.47 (−CH₂CH₂−), 114.40 (C-3), 119.22 (C-1), 122.61 (C-7), 130.88 (C-5), 134.33 (C-2), 136.89 (C-8), 135.88, 139.65, 147.22, 147.77. − UV/Vis (1,4-dioxane): λ_max (lg ε) = 246 nm (4.50), 281 (4.86), 298 (4.71) (sh), 310 (4.83), 334 (4.08) (sh), 347 (4.04) (sh), 565 (3.05), 602 (2.99) (sh), 660 (2.58) (sh). − IR (KBr): ṽ = 2860 cm⁻¹, 1602, 1575, 1430, 1390, 1360, 1320, 1250, 1190, 1065, 1015, 970, 940, 880, 830, 790, 755, 742, 726, 710, 692. − MS (70 eV); *m/z* (%): 308 (100) [M⁺], 293 (13), 291 (11), 189 (6), 279 (15), 277 (15), 265 (12), 263 (8), 252 (11), 239 (8), 215 (6), 180 (8), 178 (6), 165 (18), 154 (14), 153 (30), 152 (46), 139 (20), 127 (15), 115 (20), 65 (7). − C₂₄H₂₀ (308.4): calcd. C 93.46, H 6.54; found C 92.75, H 6.65.

Fraction 4: Yield 125 mg (6%) of **17** as blue needles, m.p. 164−165 °C (from *n*-hexane). − ¹H NMR (300 MHz, CDCl₃): δ = 2.85 (s, 3 H, 4-CH₃), 3.18 (m, 4 H, −CH₂CH₂−), 5.04 (s, 2 H, 4′-CH₂Cl), 6.98 (dd, *J₁* = 9.7 Hz, *J₂* = 1.4 Hz, 1 H, 7-H), 7.05 (dd, *J₁* = 9.7 Hz, *J₂* = 1.4 Hz, 1 H, 7′-H), 7.06 (s, 1 H, 5-H), 7.22 (d, *J* = 1.4 Hz, 1 H, 5′-H), 7.31 (dd, *J₁* = 3.8 Hz, *J₂* = 1.5 Hz, 1 H, 1-H), 7.36 (d, *J* = 3.8 Hz, 2 H, 1′-, 3-H), 7.49 (d, *J* = 3.8 Hz, 1 H, 3′-H), 7.56 (t, *J* = 3.8 Hz, 1 H, 2-H), 7.85 (t, *J* = 3.8 Hz, 1 H, 2′-H), 8.21 (d, *J* = 9.7 Hz, 1 H, 8-H), 8.23 (d, *J* = 9.7 Hz, 1 H, 8′-H). − ¹³C NMR (CDCl₃): δ = 23.14 (4-CH₃), 43.78 (−CH₂CH₂−), 46.08 (4′-CH₂Cl), 113.60 (C-3′), 114.18 (C-3), 117.09 (C-1), 117.91 (C-1′), 121.09 (C-7), 122.63 (C-7′), 124.80 (C-5′), 125.90 (C-5), 132.63 (C-2), 134.44 (C-2′, C-8′), 134.58 (C-8), 133.48, 134.68, 136.95, 138.22, 140.74, 144.30, 148.24, 149.13. − UV/Vis (1,4-dioxane): λ_max (lg ε) = 241 nm (4.60), 281 (4.81) (sh), 292 (4.99) (sh), 298 (5.05), 327 (3.93) (sh), 333 (3.99), 341 (4.01), 348 (4.07), 355 (3.88) (sh), 368 (3.09) (sh), 422 (2.22), 447 (2.24), 562 (2.88), 573 (2.88) (sh), 595 (2.85) (sh), 630 (2.68) (sh), 655 (2.51) (sh), 697 (2) (sh). − IR (KBr): ṽ = 2900 cm⁻¹, 2870, 1585, 1561, 1484, 1392, 1367, 1255, 839, 795, 746. − MS (70 eV); *m/z* (%): 344/346 (100/34) [M⁺], 309 (4) [M⁺ − Cl], 189/191 (6/1.8) [M⁺ − C₁₂H₁₁], 155 (62) [M⁺ − C₁₂H₁₀Cl], 154 (21) [C₁₂H₁₀], 153 (43). − C₂₄H₂₁Cl (344.9): calcd. C 83.58, H 6.14; found C 83.56, H 6.13.

Fraction 5: Yield 42 mg (2%) of **18** as blue needles, m.p. 178−179 °C (from *n*-hexane): − ¹H NMR (300 MHz, CDCl₃): δ = 3.22 (s, 4 H, −CH₂CH₂−), 5.03 (s, 4 H, 4-, 4′-CH₂Cl), 7.04 (dd, *J₁* = 9.7 Hz, *J₂* = 1.3 Hz, 2 H, 7-, 7′-H), 7.19 (d, *J* = 1.3 Hz, 2 H, 5-, 5′-H), 7.37 (dd, *J₁* = 3.8 Hz, *J₂* = 1.1 Hz, 2 H, 1-, 1′-H), 7.49 (d, *J* = 3.8 Hz, 2 H, 3-, 3′-H), 7.86 (t, *J* = 3.8 Hz, 2 H, 2-, 2′-H), 8.23 (d, *J* = 9.7 Hz, 2 H, 8-, 8′-H). − ¹³C NMR (CDCl₃): δ = 44.28 (−CH₂CH₂−), 46.81 (4-, 4′-CH₂Cl), 114.41 (C-3, C-3′), 118.73 (C-1, C-1′), 123.35 (C-7, C-7′), 125.55 (C-5, C-5′), 135.28 (C-2, C-2′), 135.34 (C-8, C-8′), 134.26, 138.99, 141.48, 149.47. − UV/Vis (1,4-dioxane): λ_max (lg ε) = 244 (4.58), 282 (4.80) (sh), 291 (4.95) (sh), 301 (5.05), 327 (3.87) (sh), 339 (3.97), 354 (4.01), 368 (3.29) (sh), 423 (2.05), 449 (2.08), 572 (2.87), 585 (2.88), 608 (2.84) (sh), 633 (2.77) (sh), 670 (2.47) (sh), 698 (2.26) (sh). − IR (KBr): ṽ = 2900 cm⁻¹, 2860, 1583, 1564, 1487, 1454, 1437, 1370, 1251, 1155, 1066, 992, 920, 853, 798, 689, 539, 417. − MS (70 eV); *m/z* (%): 378/380/382 (100/69/13) [M⁺], 343/345 (6/2) [M⁺ − Cl], 189/191 (37/13) [1/2 M⁺], 154 (52) [1/2 M⁺ − Cl], 153 (78), 152 (46). − C₂₄H₂₀Cl₂ (379.3): calcd. C 75.99, H 5.31; found C 75.85, H 5.31.

Fraction 6: Yield 52 mg (3%) of **16** as violet blue needles, m.p. 194−195 °C (from *n*-hexane). − ¹H NMR (CDCl₃): δ = 2.83 (m, 4 H, 10-, 10′-H), 2.87 (s, 6 H, 4-, 4‴-CH₃), 2.97 (m, 4 H, 9-, 9′-H), 3.62 (s, 4 H, 11-, 11′-H), 6.72 (d, *J* = 1.0 Hz, 2 H, 5′-, 5″-H), 6.89 (dd, *J₁* = 9.7 Hz, *J₂* = 1.0 Hz, 2 H, 7′-, 7″-H), 6.96 (dd, *J₁* = 9.7 Hz, *J₂* = 1.1 Hz, 2 H, 7-, 7‴-H), 6.97 (s, 2 H, 5-, 5‴-H), 7.29 (dd, *J₁* = 3.8 Hz, *J₂* = 1.3 Hz, 2 H, 1-, 1‴-H), 7.34−7.38 (m, 4 H, 1′-, 1″-, 3-, 3‴-H), 7.51 (d, *J* = 3.8 Hz, 2 H, 3′-, 3″-H), 7.73 (t, *J* = 3.8 Hz, 2 H, 2-, 2‴-H), 7.84 (t, *J* = 3.8 Hz, 2 H, 2′-, 2″-H), 8.21 (d, *J* = 9.7 Hz, 2 H, 8-, 8‴-H), 8.22 (d, *J* = 9.7 Hz, 2 H, 8′-, 8″-H). − ¹³C NMR (CDCl₃): δ = 24.97 (4-, 4‴-CH₃), 40.26 (C-11, C-11′), 45.77 (C-9, C-9′, C-10, C-10′), 115.33 (C-3′, C-3″), 115.97 (C-3, C-3‴), 118.88 (C-1, C-1‴), 119.08 (C-1′, C-1″), 122.89 (C-7, C-7‴), 123.03 (C-7′, C-7″), 127.54 (C-5′, C-5″), 127.68 (C-5, C-5‴), 134.43 (C-2, C-2‴), 134.80 (C-2′, C-2″), 136.10, 136.38, 138.69, 138.93, 146.05, 149.25, 150.34, 150.62. − UV/Vis (1,4-dioxane): λ_max (lg ε) = 242 nm (4.89), 281 (5.10) (sh), 288 (5.23) (sh), 293 (5.26) (sh), 298 (5.31), 326 (4.29) (sh), 333 (4.33), 342 (4.32) (sh), 348 (4.41), 420 (2.92), 441 (2.88) (sh), 557 (3.22), 575 (3.19) (sh), 600 (3.16), 658 (2.73) (sh). − IR (KBr): ṽ = 2860 cm⁻¹, 1550, 1480, 1430, 1390, 1360, 1250, 1200, 1055, 1005, 960, 835, 786, 740. − MS (FD, 0−15 mA); *m/z* (%): 618 (100) [M⁺], 309 (18) [1/2 M⁺], 119 (11). − C₄₈H₄₂ (618.9): calcd. C 93.16, H 6.84; found C 92.32, H 6.75.

Fraction 7: Yield 4 mg (0.2%) of **13** as a blue solid, m.p. 280 °C (dec.). − ¹H NMR (300 MHz, CDCl₃): δ = 3.00 (s, 8 H, −CH₂CH₂−), 3.72 (s, 8 H, −CH₂CH₂−), 6.97 (s, 4 H, 5-H), 7.03 (d, *J* = 9.7 Hz, 4 H, 7-H), 7.33 (d, *J* = 2.6 Hz, 4 H, 1-H), 7.58 (d, *J* = 3.0 Hz, 4 H, 3-H), 7.81 (t, *J* = 3.8 Hz, 4 H, 2-H), 8.23 (d, *J* = 9.7 Hz, 4 H, 8-H). − UV/Vis (CH₂Cl₂): λ_max = 246 nm, 289, 293 (sh), 298, 334, 349, 415, 445, 561, 600 (sh), 652 (sh). − IR (KBr): ṽ = 2931 cm⁻¹, 2864, 1584, 1560, 1481, 1436, 1408, 1394, 1367, 1289, 1263, 1244, 1195, 1119, 1065, 1027, 1003, 965, 939, 877, 840, 792, 749, 719, 605, 551, 419. − MS (70 eV); *m/z* (%): 616 (82) [M⁺], 462 (7) [3/4 M⁺], 461 (11), 460 (10), 308 (18) [1/2 M⁺], 307 (47), 306 (40), 305 (40), 293 (26), 292 (33), 291 (43), 154 (28) [1/4 M⁺], 153 (86), 152 (100), 151 (26), 141 (31), 139 (36), 129 (28), 128 (42), 105 (42). − HRMS: C₄₈H₄₀: calcd. 616.3130; found 616.3185.

(b) A solution of 100 ml of deprotonated **14** was prepared according to (a) from diisopropylamine (1.2 g, 12 mmol), *n*-butyllithium (1.5 M, 6.67 ml, 10 mmol) in *n*-hexane, **14** (1.24 g, 4 mmol), and THF (92 ml). This solution and a solution of tosyl bromide (1.60 g, 7 mmol) in THF (100 ml) were added dropwise to vigorously stirred THF (250 ml) at −40 °C by using the apparatus described for (a). Further treatment according to (a) gave 32 mg (3%) of **15**, 180 mg (15%) of **14**, 119 mg (10%) of **12**, 25 mg (2%) of **16**, and 10 mg (1%) of **13**.

Protonation of syn-[2.2](1,6)Azulenophane (**9A**): Solutions of **9A** were prepared in dichloromethane containing various concentrations of trifluoroacetic acid and in 30% sulfuric acid. After standing at room temp. for 3 h, the UV/Vis spectra were recorded and are listed in Table 1.

Protonation of syn-[2.2](4,6)Azulenophane (**12A**): A solution of **12A** was prepared in dichloromethane at two concentrations, about 10⁻³ M for the visible and 10⁻⁵ M for the UV spectra. Solutions of various concentrations of trifluoroacetic acid (TFA) were prepared in dichloromethane. The solution of **12A** (0.5 ml) and TFA solution (0.5 ml) were mixed in a 1-cm cell of 1 ml volume and the spectrum was immediately recorded. The results are listed in Table 2.

3-Formyl-syn-[2.2](1,6)azulenophane (**28A**): Phosphoryl chloride (35 mg, 0.23 mmol) was added dropwise to DMF (1 ml) at 0 °C with stirring. The solution was added dropwise to a solution

of **9A** (47 mg, 0.15 mmol) in DMF (10 ml). After stirring at room temp. for 2 h, the reaction mixture was poured into ice-cold water (25 ml), made alkaline with 2 N NaOH, and extracted three times with diethyl ether (25 ml). The combined organic phases were dried with magnesium sulfate and concentrated in vacuo. The residue was filtered through alumina with dichloromethane as eluent. The green eluent was concentrated in vacuo and the residue was chromatographed on alumina with *n*-hexane/diethyl ether (1:5) to give two green fractions.

Fraction 1: Yield 4 mg (9%) of **9A**.

Fraction 2: Yield 8 mg (15%) of **28A** as green crystals, m.p. 203−205°C (dec.). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.46−2.66 (m, 2 H, 11-, 12′-H), 2.85−3.01 (m, 2 H, 9-, 9′-H), 3.17−3.28 (m, 2 H, 11′-, 12-H), 3.35−3.50 (m, 2 H, 10-, 10′-H), 5.13 (dd, J_1 = 10.4 Hz, J_2 = 1.4 Hz, 1 H, 7′-H), 5.52 (dd, J_1 = 10.6 Hz, J_2 = 1.6 Hz, 1 H, 7-H), 6.46 (d, J = 10.4 Hz, 1 H, 8′-H), 6.51 (d, J = 10.5 Hz, 1 H, 8-H), 6.85 (dd, J_1 = 9.6 Hz, J_2 = 1.2 Hz, 1 H, 5′-H), 7.26 (m, 2 H, 3′-, 5-H), 7.73 (d, J = 3.9 Hz, 1 H, 2′-H), 8.06 (d, J = 9.3 Hz, 1 H, 4′-H), 8.08 (s, 1 H, 2-H), 9.25 (d, J = 10.2 Hz, 1 H, 4-H), 10.24 (s, 1 H, −C*H*O). − MS (70 eV); *m/z* (%): 336 (16) [M$^+$], 182 (12) [M$^+$ − C$_{12}$H$_{10}$], 153 (100) [M$^+$ − C$_{13}$H$_{11}$O]. − C$_{25}$H$_{20}$O (336.4): calcd. C 89.25, H 5.99; found C 88.20, H 6.26.

3,3′-Diformyl-syn-[2.2](1,6)azulenophane (**29A**): *syn*-[2.2](1,6)-Azulenophane (**9A**) (47 mg, 0.15 mmol) was allowed to react with phosphoryl chloride (70 mg, 0.45 mmol) in DMF (10 ml) as described above in the preparation of 3-formyl-*syn*-[2.2](1,6)azulenophane (**28A**). Work-up as described for the preparation of **28A** afforded 23 mg (42%) of **29A** as green crystals, m.p. 254°C (dec.). An analytically pure sample could not be obtained. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.57−2.68 (m, 2 H, 11-H), 2.84−2.98 (m, 2 H, 9-H), 3.27−3.39 (m, 2 H, 12-H), 3.43−3.53 (m, 2 H, 10-H), 5.49 (dd, J_1 = 10.5 Hz, J_2 = 1.6 Hz, 2 H, 7-H), 6.61 (d, J = 10.5 Hz, 2 H, 8-H), 7.33 (dd, J_1 = 9.9 Hz, J_2 = 1.6 Hz, 2 H, 5-H), 8.12 (s, 2 H, 2-H), 9.34 (d, J = 9.8 Hz, 2 H, 4-H), 10.32 (s, 2 H, −C*H*O). − IR (KBr): ṽ = 2929 cm^{-1} (C−H), 2700, 2720 (C−H of formyl group), 1644 (C=O), 1577 (C=C). − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 246 nm, 270 (sh), 277, 322, 394, 578, 665 (sh). − MS (70 eV); *m/z* (%): 364 (24) [M$^+$], 182 (100) [M$^+$ − C$_{13}$H$_{10}$O], 153 (21) [M$^+$ − C$_{13}$H$_{10}$O − CHO].

Aminomethylation of syn-[2.2](1,6)Azulenophane (9A): A mixture of acetic acid (0.03 ml) and paraformaldehyde (10 mg, 0.33 mmol) was heated to boiling and then cooled to room temp. A solution of **9A** (46 mg, 0.15 mmol) in benzene (6 ml) and ethanol (4 ml) was added to the above solution and then *N,N,N′,N′*-tetramethyldiaminomethane (15.3 mg, 0.15 mmol) was then slowly added dropwise. The reaction mixture was stirred at 40°C for 4 h, cooled to room temp., diluted with diethyl ether (20 ml), and extracted three times with 2 N acetic acid (10 ml). The organic phase was washed twice with water (10 ml), dried with magnesium sulfate, and concentrated in vacuo. Chromatogaphy of the residue on alumina with *n*-hexane gave 3 mg (6%) of **9A**. The combined aqueous phases were made alkaline with 5 N NaOH and a light green solid precipitated. The suspension was extracted three times with diethyl ether (30 ml). The combined ethereal extracts were dried with magnesium sulfate and concentrated in vacuo. The residue was chromatographed on alumina with diethyl ether/dichloromethane (1:1) to yield 22 mg (40%) of 3-*N,N*-dimethylaminomethyl-*syn*-[2.2](1,6)-azulenophane (**30A**) and 29 mg (46%) of 3,3′-bis(*N,N*-dimethylaminomethyl)-*syn*-[2.2](1,6)azulenophane (**31A**).

30A: Green crystals, m.p. 154−155°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.30 [s, 6 H, −N(C*H*$_3$)$_2$], 2.48−2.54 (m, 2 H, 11-, 12′-H), 2.89−3.00 (m, 2 H, 9-, 9′-H), 3.08−3.15 (m, 2 H, 11′-, 12-H),

3.35−3.45 (m, 2 H, 10-, 10′-H), 3.83−3.96 (m, 2 H, −C*H*$_2$NMe$_2$), 5.13 (dd, J_1 = 10.3 Hz, J_2 = 1.5 Hz, 1 H, 7′-H), 5.18 (dd, J_1 = 10.4 Hz, J_2 = 1.4 Hz, 1 H, 7-H), 6.33 (d, J = 10.3 Hz, 1 H, 8′-H), 6.37 (d, J = 10.4 Hz, 1 H, 8-H), 6.78 (m, 2 H, 5-, 5′-H), 7.19 (d, J = 3.8 Hz, 1 H, 3′-H), 7.68 (s, 1 H, 2′-H), 7.69 (d, J = 3.8 Hz, 1 H, 2-H), 8.03 (d, J = 9.5 Hz, 1 H, 4′-H), 8.15 (d, J = 9.7 Hz, 1 H, 4-H). − IR (KBr): ṽ = 2923 cm^{-1} (C−H), 2847, 2806, 2761 (N−CH$_3$/N−CH$_2$), 1573 (C=C). − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 247 nm (sh), 280, 300 (sh), 353 (sh), 402 (sh), 631, 665 (sh), 737 (sh). − MS (70 eV); *m/z* (%): 365 (27) [M$^+$], 321 (21) [M$^+$ − NMe$_2$], 211 (24) [M$^+$ − C$_{12}$H$_{10}$], 168 (100) [M$^+$ − C$_{14}$H$_{15}$N], 154 (36) [M$^+$ − C$_{15}$H$_{17}$N]. − C$_{27}$H$_{27}$N (365.5): calcd. C 88.72, H 7.44, N 3.83; found C 87.50, H 7.43, N 3.69.

31A: Green crystals, m.p. 133−134°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.30 [s, 12 H, −N(C*H*$_3$)$_2$], 2.48−2.50 (m, 2 H, 11-H), 2.90−2.94 (m, 2 H, 9-H), 3.10−3.12 (m, 2 H, 12-H), 3.35−3.40 (m, 2 H, 10-H), 3.82−3.96 (m, 4 H, −C*H*$_2$NMe$_2$), 5.13 (dd, J_1 = 10.2 Hz, J_2 = 1.4 Hz, 2 H, 7-H), 6.33 (d, J = 10.2 Hz, 2 H, 8-H), 6.77 (dd, J_1 = 9.7 Hz, J_2 = 1.4 Hz, 2 H, 5-H), 7.68 (s, 2 H, 2-H), 8.15 (d, J = 9.7 Hz, 2 H, 4-H). − IR (KBr): ṽ = 2925 cm^{-1} (C−H), 2848, 2805, 2762 (N−CH$_3$/N−CH$_2$), 1573 (C=C). − UV/Vis (CH$_2$Cl2): λ$_{max}$ = 246 nm (sh), 281, 302 (sh), 353 (sh), 405 (sh), 633, 675 (sh), 752 (sh). − MS (70 eV); *m/z* (%): 422 (10) [M$^+$], 378 (8) [M$^+$ − NMe$_2$], 334 (4) [M$^+$ − 2NMe$_2$], 168 (100). − C$_{30}$H$_{34}$N$_2$ (422.6): calcd. C 85.26, H 8.10, N 6.63; found C 84.44, H 8.23, N 6.22.

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