Review

Dancing with Azulene

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Abstract: It seems interesting to adopt the idea of dance in the context of the arrangement of molecular blocks in the building of molecular systems. Just as various dances can create various feelings, the nature and arrangement of molecular blocks in the generated molecular system can induce different properties. We consider obtaining such "dancing" systems in which the still little-known azulene moieties are involved. The dark blue nonbenzenoid aromatic azulene has one less axis of symmetry relative to the two axes of its isomer, i.e., the fully benzenoid naphthalene, acquiring valuable properties as a result that can be used successfully in technical applications. In a dancing system, the azulene moieties can be connected directly, or a more or less complex spacer can be inserted between them. Several azulene moieties can form a linear oligomer or a polymer and the involvement of azulene moieties in nonlinear molecules, such as crown ethers, calixarenes, azuliporphyrins, or azulenophane, is a relatively new and intensely studied topic. Some aspects are covered in this review, which are mainly related to obtaining the mentioned azulene compounds and less to their characterization or physico-chemical properties.

Keywords: azulene; linear and nonlinear oligomers and polymers

1. Introduction

In a dance, one to several participants may be involved. They can evolve in multicolored costumes in all kinds of formations, for example, two or more, in a chain or a circle. It seems interesting to adopt the idea of dance in the context of the arrangement of molecular blocks in the building of molecular systems; obviously, the blocks can be identical or different. Just as various dances can create varied feelings, the nature and arrangement of molecular blocks in the generated molecular system can induce quite different properties. Herein is described the obtaining of such "dancing" systems in which the colored azulene moieties (see Scheme 1) are involved without insisting on their properties and use, except for a few interesting pieces of information. Nonbenzenoid aromatic azulene has one less axis of symmetry compared with its benzenoid isomer naphthalene (Scheme 1). Although this difference decreases the stability of the azulene system, valuable properties are acquired that can be successfully used in technical applications. In a dancing system, the azulene moieties can be connected directly or a more or less complex spacer can be inserted between them.

The spacers described in the literature may provide a conjugation between the linked azulene, such as a double carbon bond or *para* positions of the benzene ring; Csp^3, Csp^2 atom, NH group, etc. can also be encountered as spacers. Several azulene moieties can form a linear oligomer or a polymer (compounds with structure **A** or **B** in Scheme 1). The involvement of azulene moieties in nonlinear molecules, such as crown ethers (compounds **C**), azulenophanes (compounds **D1** and **D2**), calixazulenes (compounds **E**), or azuliporphyrins (compounds **F**) and similar derivatives (compounds **G**), is relatively new and intensely studied. The binding position of azulenes can be identical or different, leading to an impressive number of possible molecules. The use of the same positions or positions 2 and 6 (see Scheme 1) creates symmetry for the resulting large π-electron system with remarkable consequences on their properties. In turn, the asymmetric binding ensures the asymmetry

of the electronic system. From the multitude of possible "dancing" azulene compounds that have been produced and studied so far, herein the interest is directed only at some less common compound classes, avoiding the classics presented extensively in the literature [1]. The review was designed mainly with the intention of highlighting the wide variety of compounds that have azulene in their structure and to show how they were obtained.
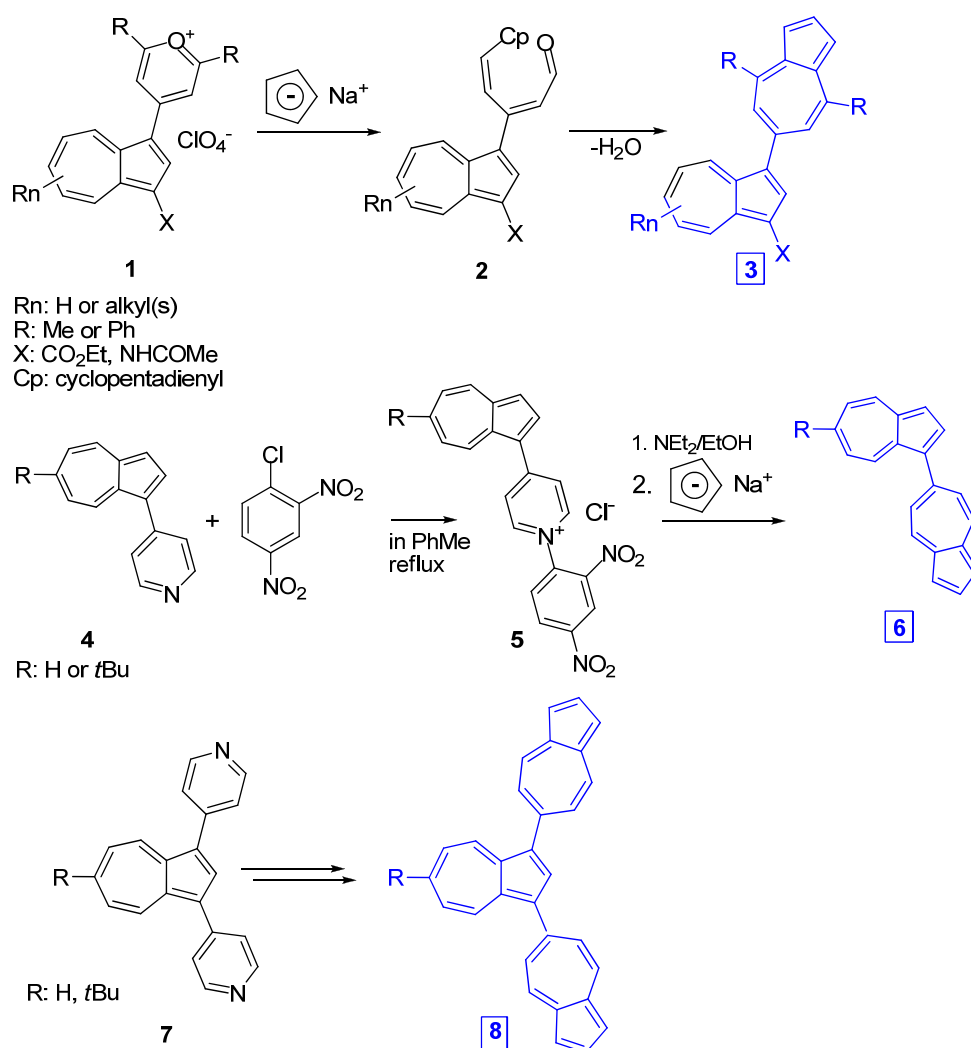

Scheme 1. "Dancing" systems containing azulene moieties.

2. The Dance of Two or More Azulenes without Any Spacers ("Dancing Groups" A)

The enormous number of compounds containing two-connected azulenes that were obtained and studied over time is due to the number and nature of azulene substituents and to the positions used to link the participants. Usually, the synthesis of symmetrical biazulenyl derivatives that are coupled in identical positions occurs easily. However,

when the coupling positions have very different electron charges, the synthesis pathway is more difficult. The *annulation process* and *the coupling of two azulenes* are the main routes for the preparation of biazulenyl-containing "dancing systems" of type **A1** and even **A2** (Scheme 1).

Several biazulenyl compounds, for example, the 5,5'- or 6,6'-coupled azulenes, which result from the cyclopentadiene *annulation*, follow the Ziegler–Hafner reaction [2]. Recently, the research teams of Razus [3] and Ito [4] obtained the unknown 1,6-coupled azulenes using the annulation. As described in Scheme 2, starting from pyranylium salts, the first team obtained the product in one step, whereas two steps were required starting from pyridinium salts by the second team. As it can be seen from Scheme 2, the last route allowed for obtaining product **8** of type **A2**.
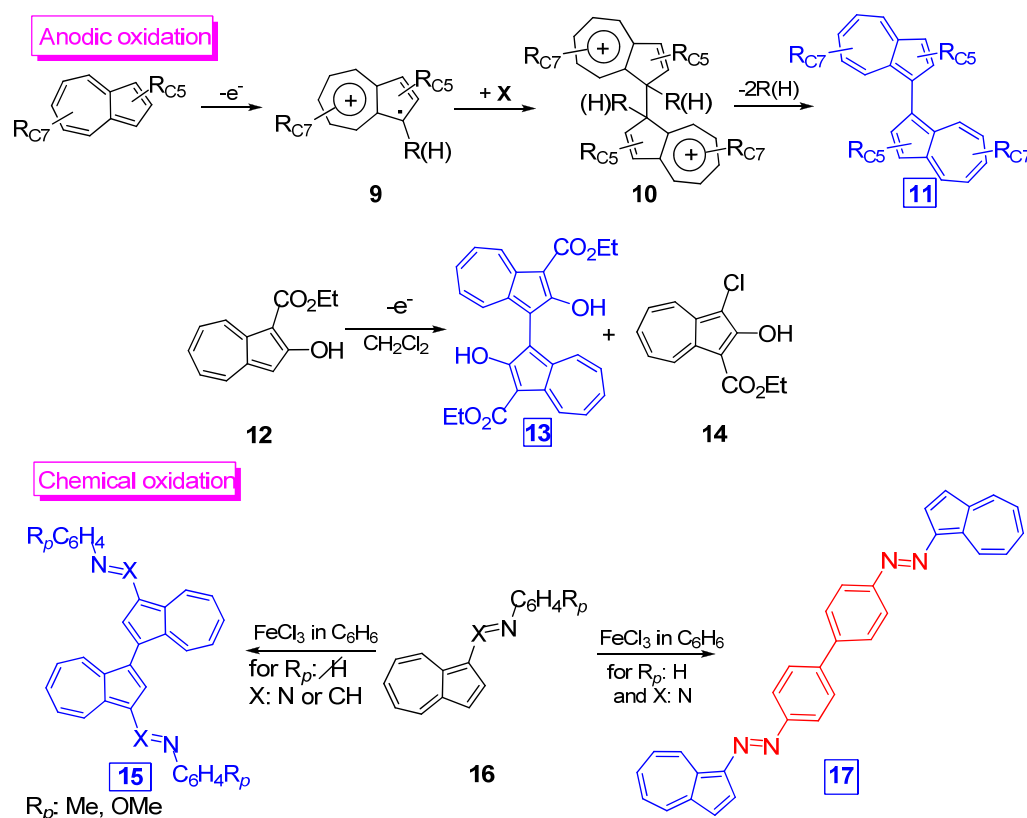

Rn: H or alkyl(s)
R: Me or Ph
X: CO_2Et, NHCOMe
Cp: cyclopentadienyl

R: H or *t*Bu

R: H, *t*Bu

Scheme 2. Cyclopentadiene annulation following the Ziegler–Hafner route.

The more commonly used *coupling process* between azulenes can be realized through different routes and it is not the purpose of this review to exhaust all the material published in this field. Only several coupling reactions chosen based on the historical criterion or due to the interest presented by the synthesized products are presented.

(a) Old Ullmann condensation or dimerization to 1,1'-, 2,2'-, 1,2'-, or 2,6'-biazulenes and their derivatives were realized using the corresponding halogenated azulenes in the presence of activated copper in a sealed tube. Starting from a mixture of 1-bromo and 1,3-dibromoazulenes in the presence $NiCl_2/(Ph_3P)_2$, Zn, and Et_4NI (in THF) [5], a mixture of 1,1'-biazulene and azulene oligomers was obtained [6].

(b) Electrochemical anodic oxidation [7,8] or chemical oxidation [9–11] of 1-substitued azulene. Due to the possibility to stabilize the positive charge as a tropylium moiety (intermediate radical cation **9**), the azulene structure is favorable for one-electron elimination, as shown in Scheme 3. Thus, the electrochemical electron transfer gave compound **13**, and compound **15** was generated when FeCl$_3$ was used as the oxidant for compound **16**. However, when the phenyl is not substituted at position 4 in compound **16**, the coupling was directed in this position, which was more reactive than the azulene position 1, consequently, the "biazulene **17′**'' was produced with a biphenyl spacer.
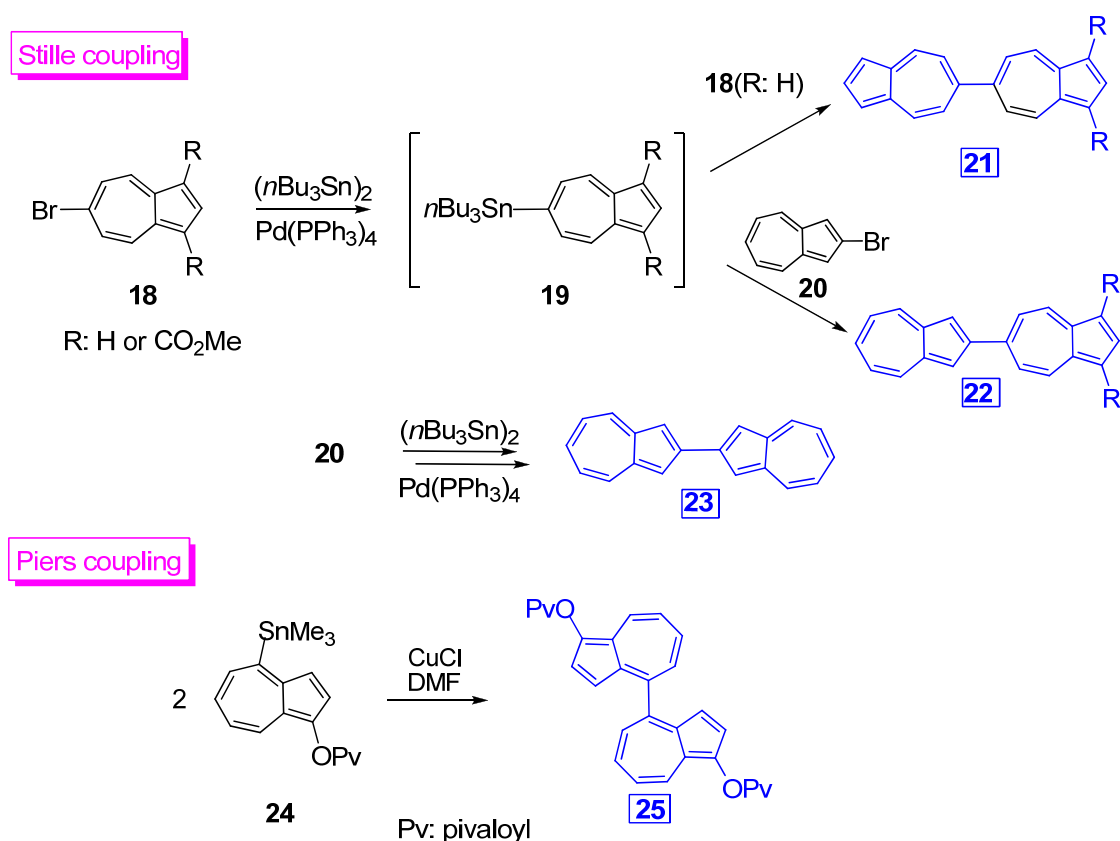

Scheme 3. Oxidative dimerization.

(c) Photoirradiation coupling of 1-azulenyl iodide with azulene in hexane [12]. The reaction proceeds regioselectively at the electron-rich 1-position with the elimination of iodine (azulene conversion 28%; yield 67%).

(d) Palladium-catalyzed intermolecular arylation of unsubstituted azulene [13]. Surprisingly, in an attempt to generate the azulene-Pd complex starting from azulene and palladium acetate, the 1,2′-biazulene was produced in a 10% yield.

Several *cross-coupling reactions* were also reported and were applied to obtain biazulenyl compounds of type **A1**; most of these reactions are transition-metal-mediated.

(a) The cross-coupling reaction of the organotin derivatives with electrophiles is palladium-catalyzed, known as the Stille reaction for carbon–carbon bond formation, was applied by Ito et al. [14] for the preparation of compounds **21** and **22**. The reaction started from the 6-substituted azulenes with *n*Bu$_3$Sn and azulenes with Br in 6 or 2 positions (Scheme 4). After several reaction steps, 2,2′-bisazulene **23** was also obtained with a good yield.
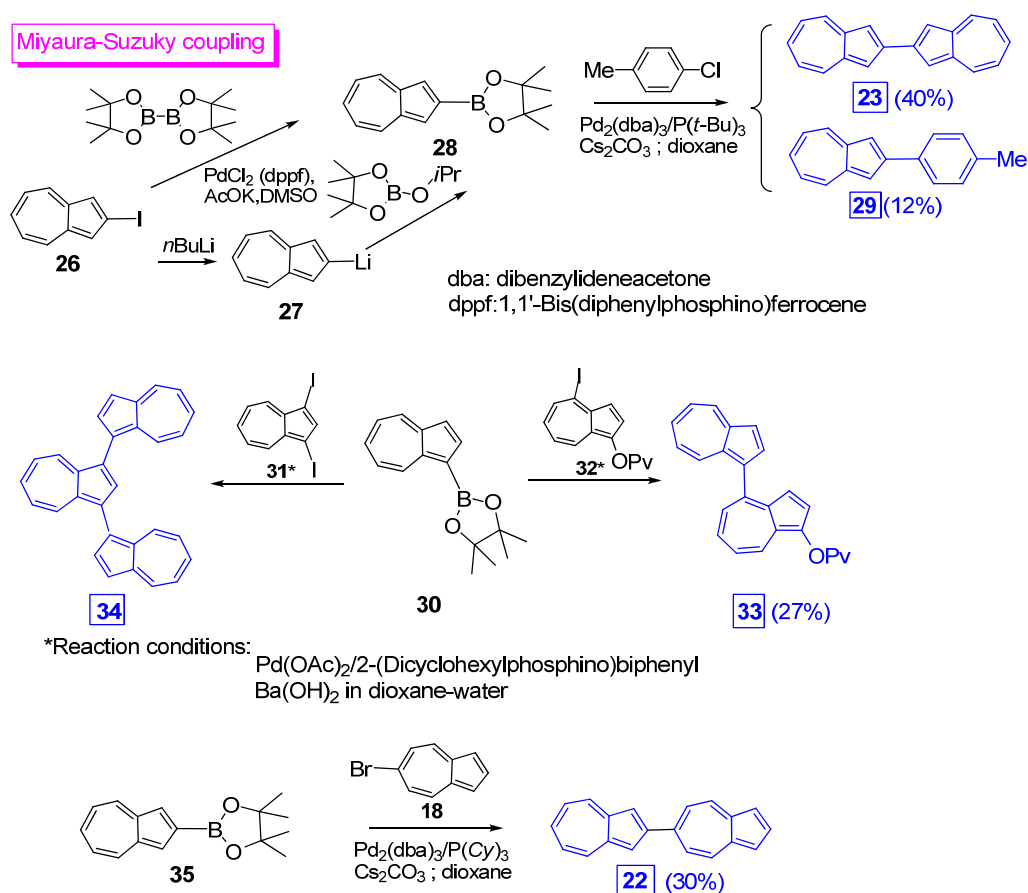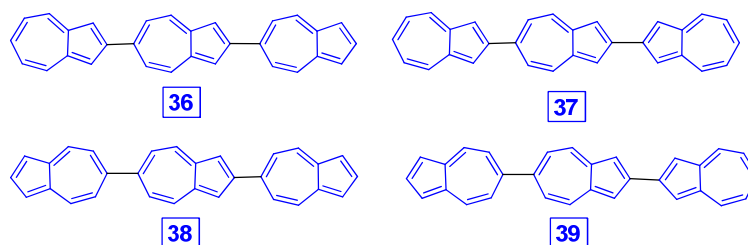
Scheme 4. Stille and Piers coupling.

(b) The Piers variant [15] of the Stille reaction [16] in the presence of CuCl allowed for the synthesis of 4,4′-coupled azulene **25**.

(c) The Miyaura–Suzuki reaction of 1-azulenyl boronate with halogenoazulene derivatives [16,17]. Scheme 5 describes the route toward the azulenyl boronates **28** and **30** and their reaction with halogenoazulenes in the catalytic presence of palladium complexes. The bisazulenes **23** and **33** were produced in moderate yields from these reactions. Ito and colleagues reported the unexpected 2,2′-bisazulene formation as a major product, together with 2-(4-tolyl)azulene **29** in the reaction of boronate **28** with 4-chlorotoluene, whereas, using brominated toluene, the compound **29** was the only product. In similar reaction conditions, the azulene trimer **34**, belonging to the compounds of type **A2**, was generated [16].
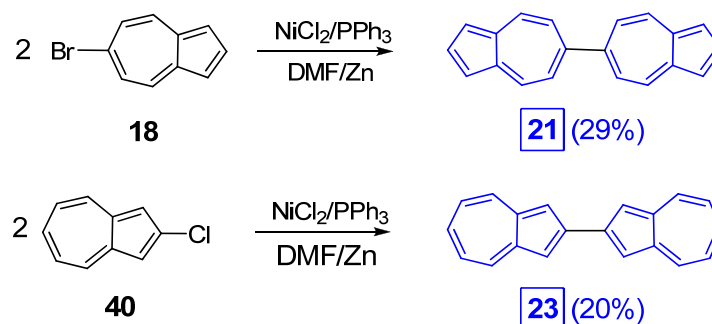
A series of biazulenes and terazulenes of type **A1** and **A2**, presumed to have valuable technical properties (biazulenes **22** and **23**, and terazulenes **36–39** from the Scheme 5) were produced after a sequence of Miyaura–Suzuki condensations [18,19]. The compounds **21** and **23** were also obtained by starting from the appropriate halogenated derivatives **18** and **40** in the nickel complex catalysis (Scheme 6) [20].

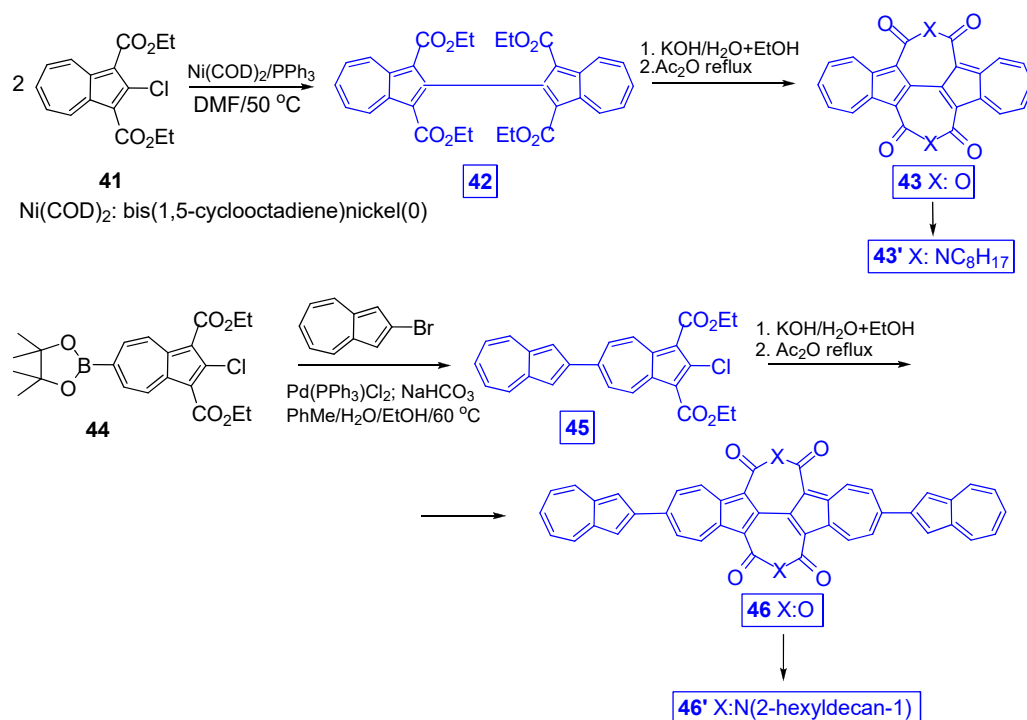**Scheme 5.** Miyaura–Suzuki reaction of azulene-1-yl boronate.

Scheme 6. Nickel-complex-promoted coupling.

The effects of the molecular and packing structure of some linear biazulenes on the optoelectronic and charge-transport properties were studied, demonstrating the importance of molecular structure and orbital symmetries [20]. Thus, 2,2′-biazulene **23** and 2,6-connected
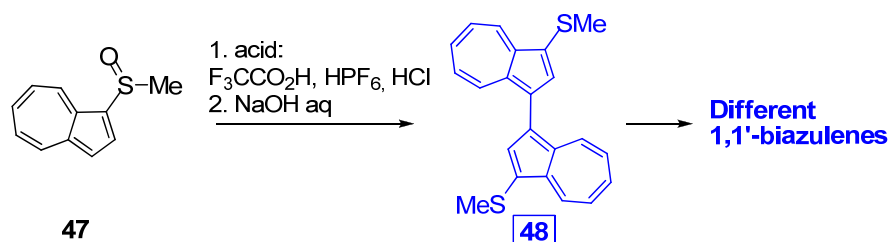
terazulene **36** possess properties of high-performance organic field-effect transistor (OFET) materials, and the alternating seven and five rings in the dimer **22** or trimer **36** favors potential NLO (nonlinear optical) features.

A somewhat more complicated bisazulenic system with valuable photophysical properties and are promising for organic electronic materials, namely, the 2,2′-biazulene-1,1′,3,3′-tetracarboxylic diimides **43′** and **46′**, contain a 2,2′-bisazulene moiety [21,22]. The 2,2′-bisazulene **42** was produced via the dimerization of 2-chloroazulene **41** and the subsequent steps generated anhydride **43** and, finally, the diimide **43′**. The same valuable properties were reported for compound **46′** with four coupled azulenes synthesized, as described in Scheme 7.

Scheme 7. Synthesis of dianhydride **43** and **46**, which were used as precursors of the corresponding diimides **43′** and **46′**.
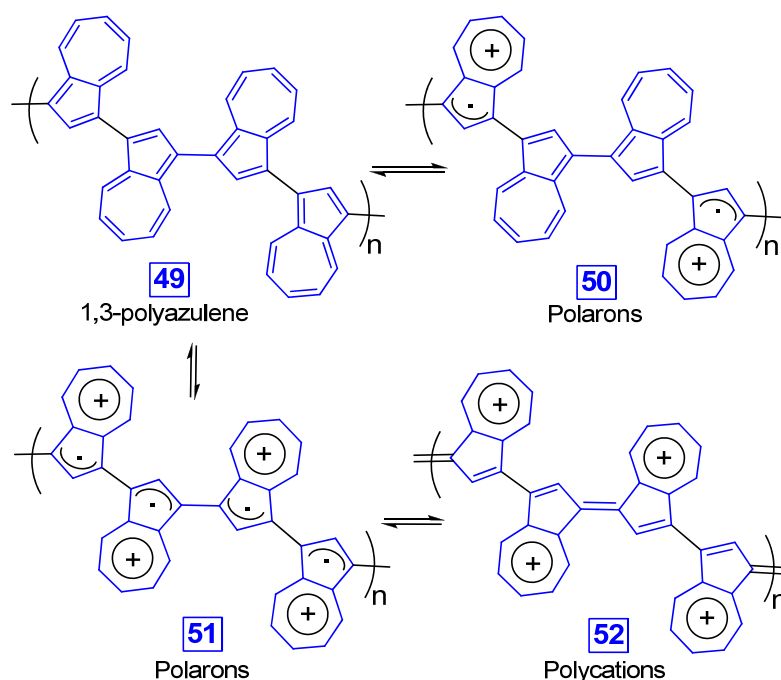
The coupling of two azulenes (**47**) in position 1, avoiding the transition metal catalysis [23,24], is worth examining. The used reaction steps are shown in Scheme 8 and the importance of the described procedure consists of the multitude of compounds that can be derived from compound **48**. Interestingly, the proposed dimerization mechanism involves the azulene radical cation as the intermediate (see Scheme 3).

Scheme 8. Coupling of two azulenes in position 1, avoiding the transition metal catalysis.

At the end of this chapter, another member of the "dancing chain group" is mentioned, namely, polyazulene, due to its interest as a material with optical and electrical properties for the design of molecular devices. From the countless number of studies undertaken in this field, only a few representative ones will be selected. The chemical synthesis of

electroactive and partially soluble polyazulene was realized via the chemical oxidative polymerization of azulene with iodine and bromine [25], with FeCl$_3$ [26], or via the polymerization of 1,3-dibromoazulene with Ni(COD)$_2$ [27]. Electrochemical polymerization was also used with significant results [28,29]. The electronic and structural properties of azulene-based polymers [30] and their optoelectronic and energy applications [31] were carefully investigated. After polymerization, the azulene units remain unchanged when coupling occurs in the 1,3 positions, as described in Scheme 9 for polyazulene **49**. Remarkably, the protonation of 1,3-polyazulene by trifluoroacetic acid has high conductivity and paramagnetic property+es as a result after the generation of radical cations **50** and **51** (polarons); by increasing the acidity, polycations **52** were formed [27,30].

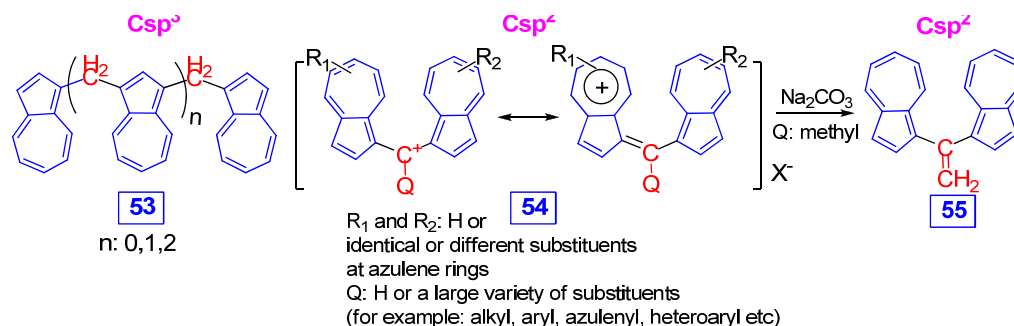**Scheme 9.** The behavior of polyazelune in the acidic medium.

Very recently, the polymerization of azulene in positions 2,6 was successfully carried out and the interesting properties of the afforded polymer for the application as functional materials were studied. The new "on-surface synthesis" developed as a complementary strategy for chemical synthesis was used for generating homopolymers starting from 2,6-diiodoazulene [32] or 2,6-dibromoazulene [33] on Au[111].

3. The Dance of Two or More Azulenes with Various Spacers ("Dancing Groups" B and C)

Although examples of compounds in which a wide variety of azulenes are directly related to each other are far from exhausted, we move on to compounds with spacers interspersed between azulenes (Scheme 1). In these compounds, in addition to the multitude of azulene building blocks, there is a large variety of spacers that can be present. This specific feature and the scientific and applied interest presented by these compounds have led to an intense interest in the field. The characteristics and importance of this type of molecule were examined in several articles and a review published in 2020, which lists some recent information about such systems [34]. Therefore, in this section, only a few relevant aspects related to the compounds of "dancing" groups **B** and **C**, especially those related to the compound synthesis, will be highlighted.

First, substituted Csp^3 and Csp^2 can be mentioned as very simple spacers (Scheme 10). The coupling of 1-iodide in DMF at 85–90 °C afforded a mixture of 1-azulenmethylene oligomers **53**, with saturated carbon as a spacer [35]. The involvement of a Csp^2 atom near the azulenyl moieties in compounds of type **B** and **C** was largely discussed in a published

review by Razus in the *Symmetry* journal [36]. Thus, the electron donor property of azulene as a stabilizer for the positive charge as in compounds **54** was emphasized. However, the presence of a Csp^2 atom belonging to ethene between two azulenes as in compound **55** after cation **54** (Q = methyl) stabilization is interesting [37].
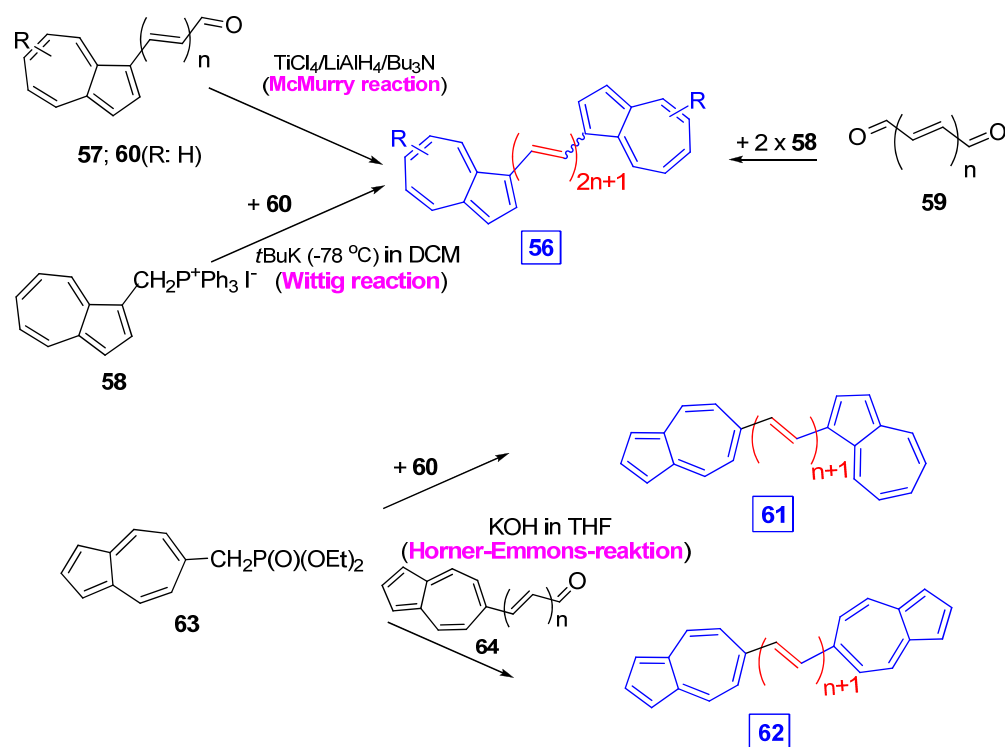

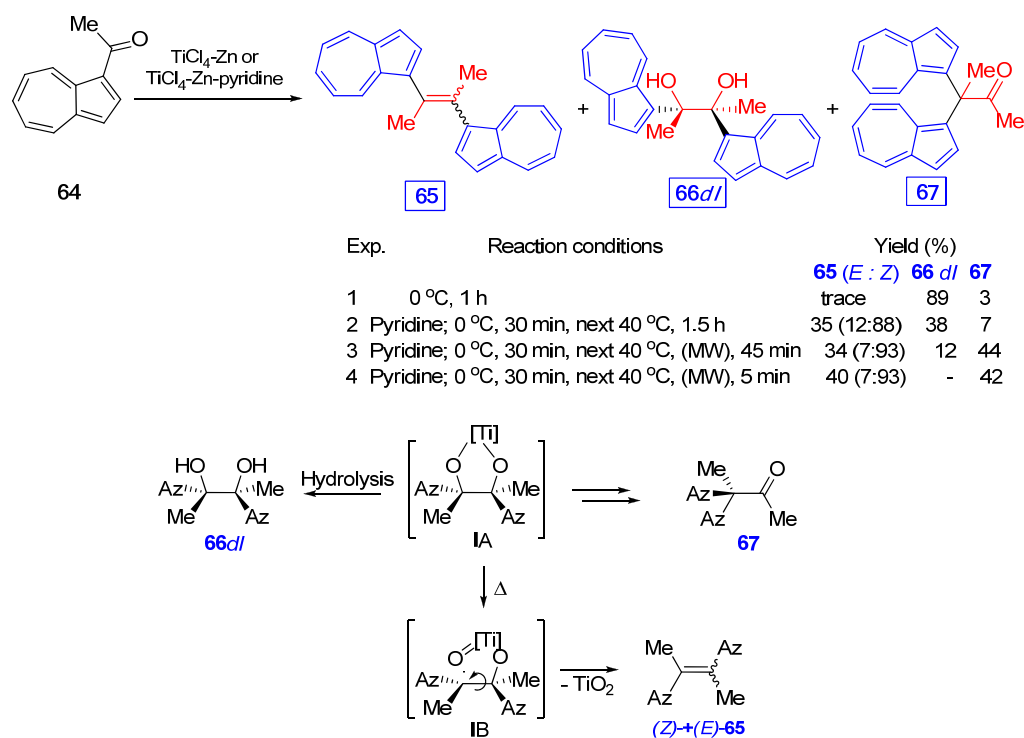**Scheme 10.** Csp^3 and Csp^2 as a spacer between azulene moieties.

An extensive discussion in azulene chemistry is focused on the study of C=C bond(s) substituted with azulene. The interest is related to the possibility of these compounds working as a metal due to their insignificant oxidation potentials. In Scheme 11, the important classical procedures for the synthesis of 1,2-biazulenyl ethenes and α,ω-biazulenyl polyenes [38] are depicted. For the less common isomers with the azulene coupled in 2,6 or 6,6 positions, namely, **61** or **62**, Hunig and Ort used the Horner–Emmons reaction of phosphonate **63** with aldehydes with success [1]. The coupling in the 2,2 positions (compound **56**) was realized using the Wittig route, starting from phosphonium salt **58** and corresponding aldehydes in severe reaction conditions and with moderate-to-good yields [1]. A more favorable reaction was shown to be the McMurry condensation between two aldehydes (**57** or **60**) catalyzed using Ti(0) from the perspective of the reaction conditions, as well as from the yields obtained. However, insufficient data on the mechanism of the last condensation procedure suggests the need for enlargement of the research on this topic [39]. At the beginning, 1-acetylazulene reacted in the presence of $TiCl_4$–Zn and the results are described in Scheme 12.

The pyridine was added in several experiments and a series of attempts were performed that involved heating the reaction mixture under microwave irradiation. Surprisingly, a mixture of alkene **65** and pinacol **66** and the product of pinacol/pinacolone transposition **67** were produced in a ratio that depended on the reaction conditions, as described in Scheme 12. The proposed mechanism, based on the reaction results, which postulates the structures **IA** and **IB** as intermediates, is also summarized in Scheme 12.
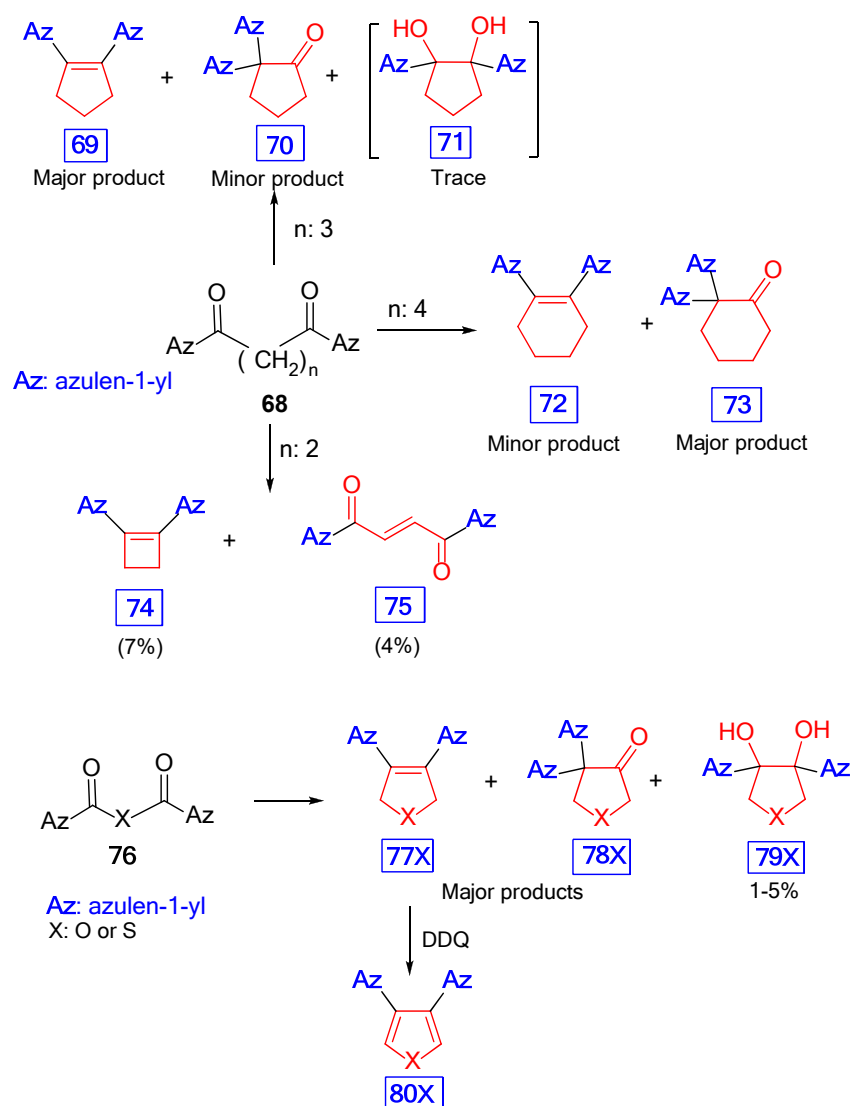
The interesting results obtained encouraged the extension of the reaction to intramolecular condensation [40,41]. Thus, a series of carbocycles and heterocycles comprising 1,2-diazulenylethene moieties **69**, **72**, and **74** (Scheme 13), which are difficult to obtain from other reaction routes, was synthesized. The reported results highlight the decisive influence of azulene substituents on the product mixture, in addition to the reaction conditions. As a general tendency, the preponderance of alkene and pinacolic transposition compounds in the product mixture to the detriment of the pinacole can be observed. As expected, the closing of the four-atom ring with a double bond (compound **74**) was found to be particularly unfavorable such that cyclobutene was obtained only with a yield below 10%. Unfortunately, a broader discussion on these topics cannot be developed in this review. An advantage of the described McMurry route consists in the possibility to generate heteroaromatic furan and thiophene **76** (X = O or S) starting from the corresponding alkenes **77** (X = O or S) (Scheme 13) [40].

Scheme 11. α,ω-Biazulenyl polyenes syntheses (C=C present as a spacer(s)).

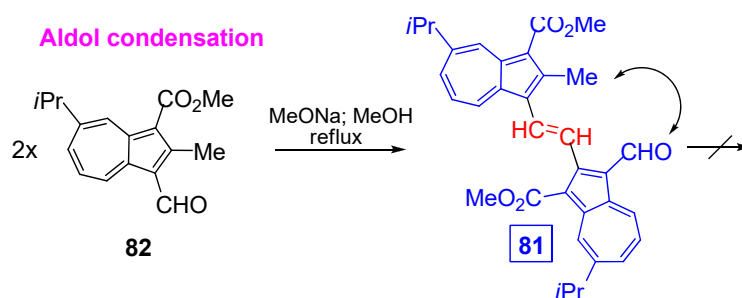| Exp.	Reaction conditions	65 (*E* : *Z*)	66 *dl*	67
1	0 °C, 1 h	trace	89	3
2	Pyridine; 0 °C, 30 min, next 40 °C, 1.5 h	35 (12:88)	38	7
3	Pyridine; 0 °C, 30 min, next 40 °C, (MW), 45 min	34 (7:93)	12	44
4	Pyridine; 0 °C, 30 min, next 40 °C, (MW), 5 min	40 (7:93)	-	42

Scheme 12. McMurry reaction of 1-acetylazulene in the presence of TiCl$_4$–Zn or TiCl$_4$–Zn–pyridine.
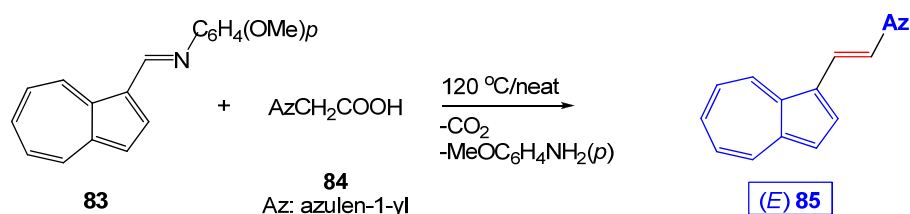
Scheme 13. McMurry intramolecular coupling.

In an attempt to synthesize cyclooctatetraene derivative fused by two azulenes, Shoji et al. tried closing the ring in the intermediate ethene **81** substituted with two azulenes (Scheme 14) [42]. This intermediate resulted in an aldol condensation between carbonyl in position 1 and methyl in position 2 of the azulene compound **82**.

Scheme 14. Aldol condensation between carbonyl and methyl substituents at the azulene.
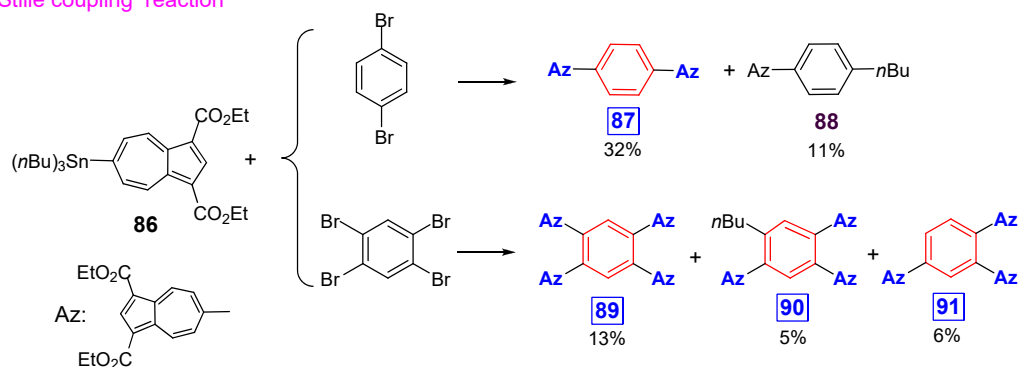
In a comprehensive article on substituted 1-azulenylethenes, the condensation of a Schiff base with 1-azuleneacetic acid produced 1,2-diazulenylethene (Schiff base conversion 40% and yield 81%) (Scheme 15) [43].
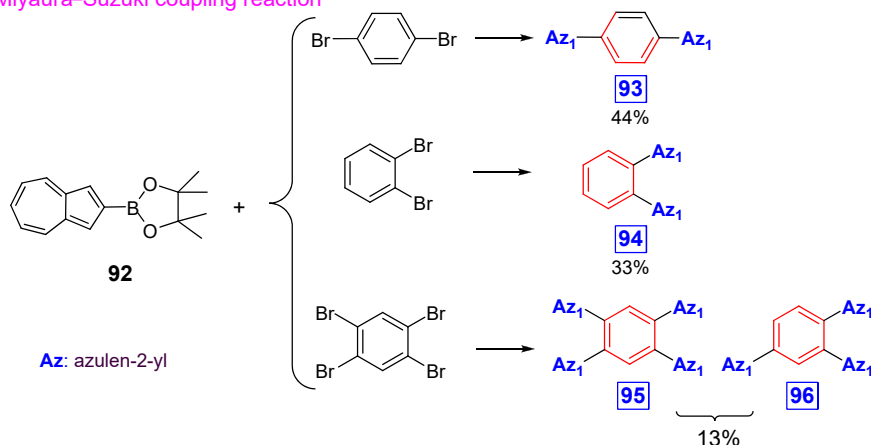
Scheme 15. Condensation of a Schiff base with 1-azuleneacetic acid.

The substitution of positions 1,2 or 1,4 in benzene ensures a continuous conjugation of the substituents grafted in these positions. Scheme 16 provides some examples of the benzene spacer substituted with 2- or 6-azulenyl groups. For the preparation of products, the already described procedures, namely, Stille and Miyaura–Suzuki coupling, were considered [14,17]. Interestingly, the condensations afforded, together with the attempted compound, the product of substitution with *n*Bu and even that which resulted after bromine elimination, i.e., compounds **88**, **91**, and **96**, respectively. The yields of products were between moderate and low. The Miyaura–Suzuki reaction proceeded better, although the polysubstituted products resulted in a reduced amount.
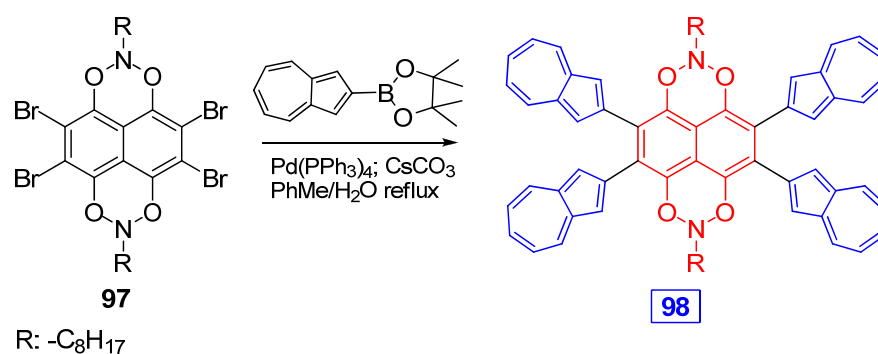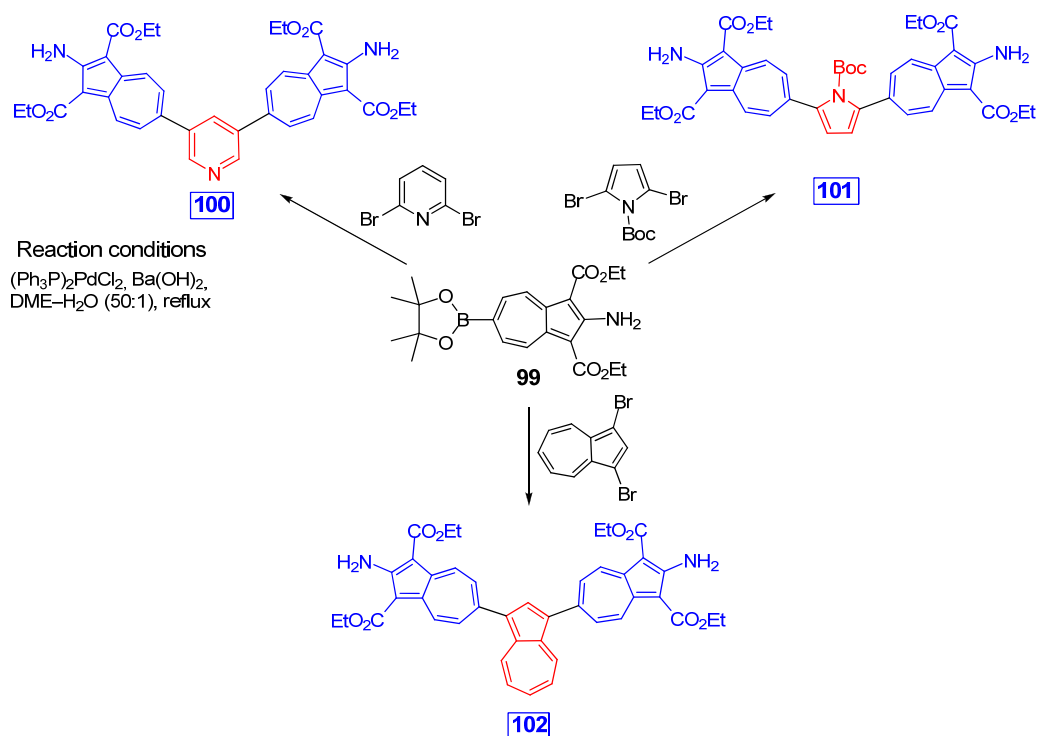

Scheme 16. Benzene as a spacer between azulene moieties.

Naphthalene as a spacer was also found in the literature, and in Scheme 17, the synthesis of such a product is exemplified [44]. The azulenophthalimides as the compounds **64′** and **98** displayed a significant spectral change under electrochemical reduction conditions, which are interesting for technical applications.
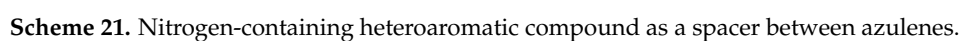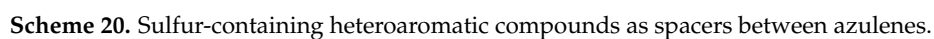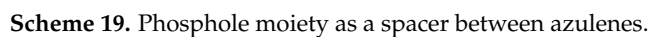
Scheme 17. Naphthalene as a spacer between azulene moieties.

Aromatic heterocycles can also play the role of a spacer between azulene. Several optoelectronic and energy applications of such compounds were presented in a review published in 2020 [31]. One example was already given in Scheme 13, namely, the furan and thiophene **80** (X = O and S). Examples of pyridine or pyrilium compounds **100** and **101** were obtained using the Miyaura–Suzuki route, as described in Scheme 18, starting from the corresponding dibromide derivatives [45]. Scheme 18 also provides an example of the synthesis of terazulene **102** with the central azulene substituted in position 2 with 6-azulenylazulene.

Scheme 18. Aromatic heterocycles substituted by azulenes.

From the large number of compounds containing a heteroaromatic spacer between azulenes, a few are highlighted only as prototypes because a comprehensive review about this series of compounds has recently appeared [34,46]. In Schemes 19–21, there are several examples of such compounds with their synthesis. The phosphole compound **104** was obtained using the Stille coupling method, starting from 2,5-bis(tri-*n*butylstannyl)phosphole **103** (Scheme 19) [47].

Scheme 19. Phosphole moiety as a spacer between azulenes.

Scheme 20. Sulfur-containing heteroaromatic compounds as spacers between azulenes.

Scheme 21. Nitrogen-containing heteroaromatic compound as a spacer between azulenes.
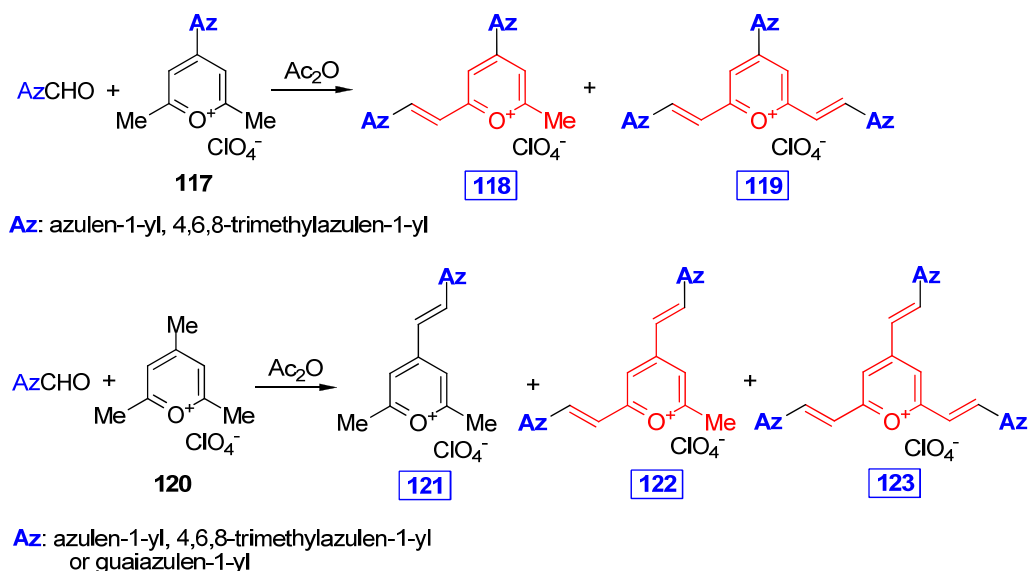
More commonly encountered are the compounds with sulfur-containing heterocycle(s) as spacers (Scheme 20) due to their potential use in electronic devices based on their features in organic field-effect transistors (OFETs) [48].

The reaction route for the generation of compound **106** starts from 3,4-ethylenedioxythiophene (EDOT) **105** and occurs in two successive steps with mono and second substitution of a thiophene ring (yield 81%). Other compounds with thiophene spacer(s), namely, **107–109**, were achieved in the same way with excellent yields. The same technical application was also assumed for compounds **111** and **113**. For the first compound, Stille condensation of bis-stannane **110** with azulene was used [16], and Miyaura–Suzuki condensation of thienothiophene diboronic acid ester **112** with 2-iodoazulene afforded the product **113** (Scheme 20) [49].

The quatropolar acceptor–donor–acceptor dye structure of compounds **115** and **116** with a pyrrolo[3,2-b]pyrroles spacer between azulenes stimulated the synthesis of these products (Scheme 21). The chosen pathway was different from those discussed for the analog sulfur-containing compound **113** and followed the building of azulene moieties accordingly the Ziegler–Hafner route [50] described above [2].
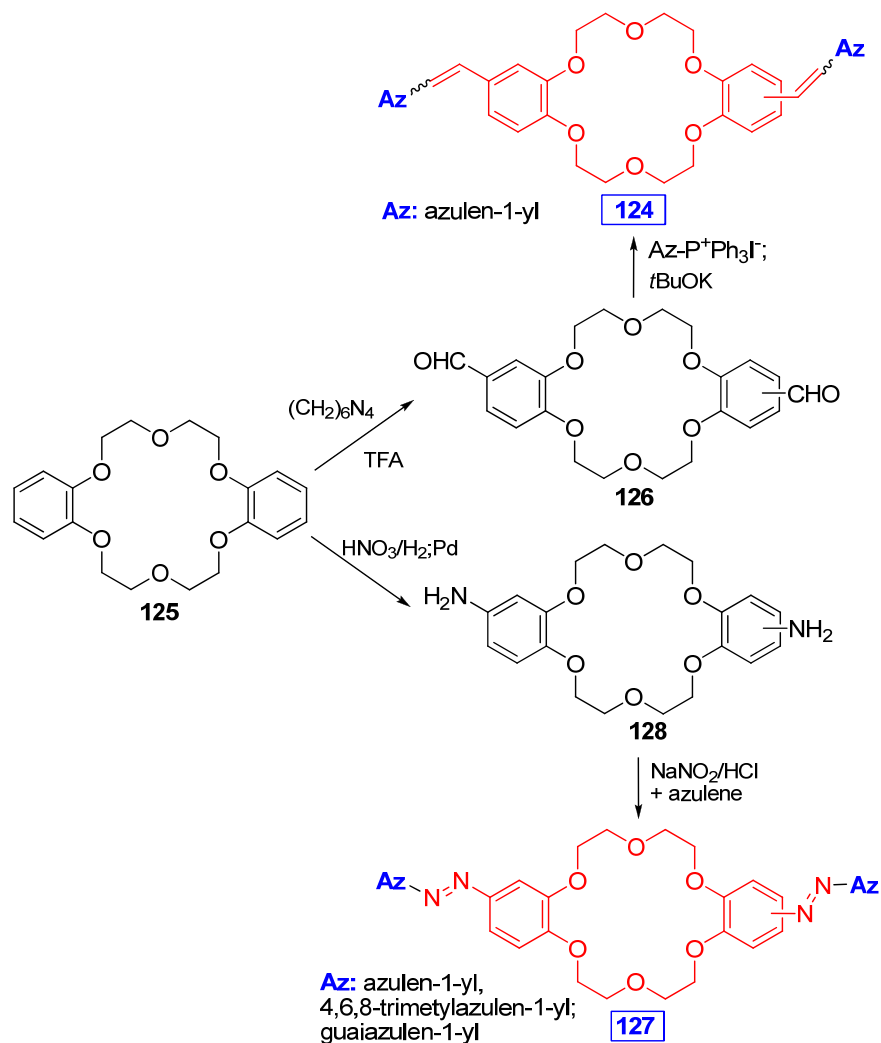
The ability of azulene to stabilize positive charge suggested to Razus et al. the use of this moiety to increase the stability of the heteroaromatic cations as such for pyrylium and pyridinium salts. The obtained results were reported in a detailed review [51]; therefore, only a few data on these studies are presented in Scheme 22. The syntheses are based on the condensation of aldehydes with a reactive methyl group in the presence of a dehydrating agent as acetic anhydride [51]. The reaction of 1-azulencarbaldeydes with 2,6-dimethyl substituted 4-(azulen-1-yl)pyrylium salt **117** affords a mixture of products. A mixture of products also provided the reaction of 2,4,6-trimethylpyrylium salt **120**. Both series of products contain the pyryliumvinyl(s) moieties as spacers. The total yields were good, but only traces of completely condensed products **119** or **123** were formed after heating the reaction mixture. However, microwave-assisted reactions selectively generated the fully condensed compound.

Scheme 22. Pyrylium vinyl cation as a spacer between azulenes.

An interesting class of spacers includes the crown ethers, which are known for their use in chemical and biomedical purposes. Because they are colorless, the introduction of the azulene chromophore in the structure ensures a color that allows their easier detection. An example of the introduction of azulene into the crown ether ring was described by Löhr et al. [52]. The dibenzocrown ether **125** was used as a support for the azulene moieties and the connection between them was realized with spacer C=C or N=N bonds, as described in Scheme 23. The

bisvinylazulene **124** was achieved via the Wittig route, starting from the dibenzocrown **125**, by passing through the dialdehyde intermediary **126** [53]. The bisazoderivatives **127** was produced via diazotization of the intermediate diamine **128** [54]. Unfortunately, the reaction starting from compound **125** does not work regiospecifically and the condensation with aldehyde occurred with the generation of both geometric isomers. However, for several practical applications, this does not seem to be a problem. The reported yields for both reactions were good to moderate.

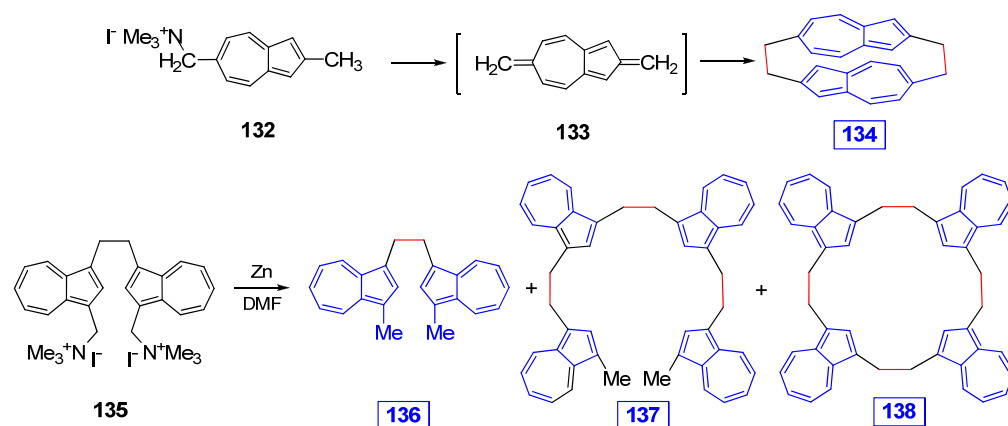**Scheme 23.** Benzocrown ethers with 1-azulenylvinyl or azulenylazo substituents.

In large reviews of azulene compounds with importance in the field of optoelectronics [31,55], the authors focused their concerns also on azulene-based copolymers with different spacers. The non-alternant structure of azulene induces a small HOMO–LUMO bandgap with beneficial consequences on the practical applications of compounds containing azulene(s), for example, for NLO devices. According to their structure, these compounds can also be considered as belonging to category "chain dancing group" **B2**, as shown in Scheme 24, which contains some examples of such structures. The polymers were obtained via chemical [56–58] or electrochemical routes [59] (polymers **129–130** or polymer **131**, respectively). Several among the attempted chemical syntheses for achieving dimers or oligomers were aforementioned. Azulene-containing polymers have also attracted interest in the fields of materials chemistry and pharmaceutical sciences. However, a more detailed treatment of these subjects exceeds the intended purpose of this review.

Scheme 24. Azulene-based copolymers.

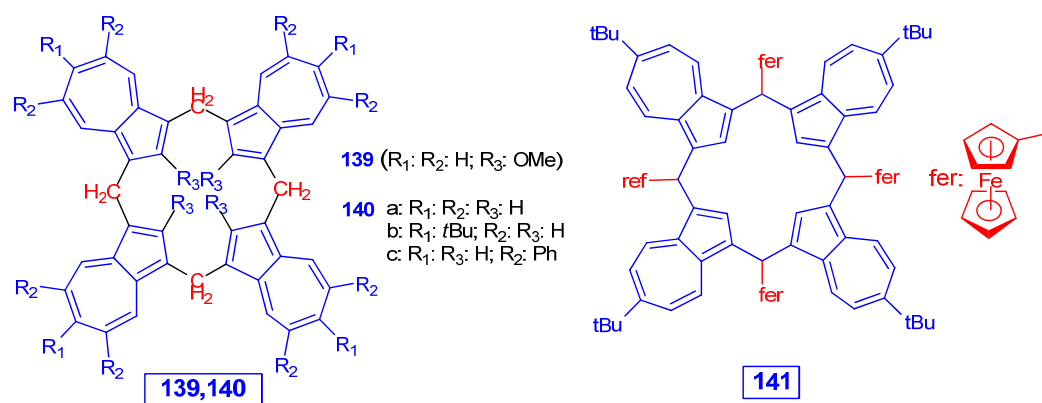### 4. The Dancing Circle Groups ("Dancing Groups" D and E)

This section surveys a few interesting pieces of information, although older, on anti-[2.2](2,6)-azulenophane **134** (Scheme 25) [60,61] and [2.2.2.2](1,3)-azulenophane **138** [35]. It seems strange that the azulenophane **134** in which two dipolar rings are facing each other did not receive more attention. The Hofmann pyrolysis of salt **132** afforded the target compound **134** through the intermediate **133**; however, the yield was 9–11%.

Scheme 25. Azulenophanes.

As it can be seen, compound **138** belongs to the "dancing circle group" (Scheme 1) while compounds **136** and **137** belong to "the chain group." The double salt **135** in DMF in the presence of Zn powder formed a high amount of polymer; however, after careful processing of the reaction mixture, the compounds **136–138** were separated in amounts that only allowed for the products' characterization (yields ~1%).

In contrast, the tridimensional calixazulenes (Scheme 26) received much more attention and a recent comprehensive paper, where Georghiou et al. deals extensively with this topic [62]. The supramolecular relationships between bowl-shaped calixarenes and the fullerenes with the potential for encapsulating C_{60} or C_{70} fullerenes have stimulated the interest of chemists [63].
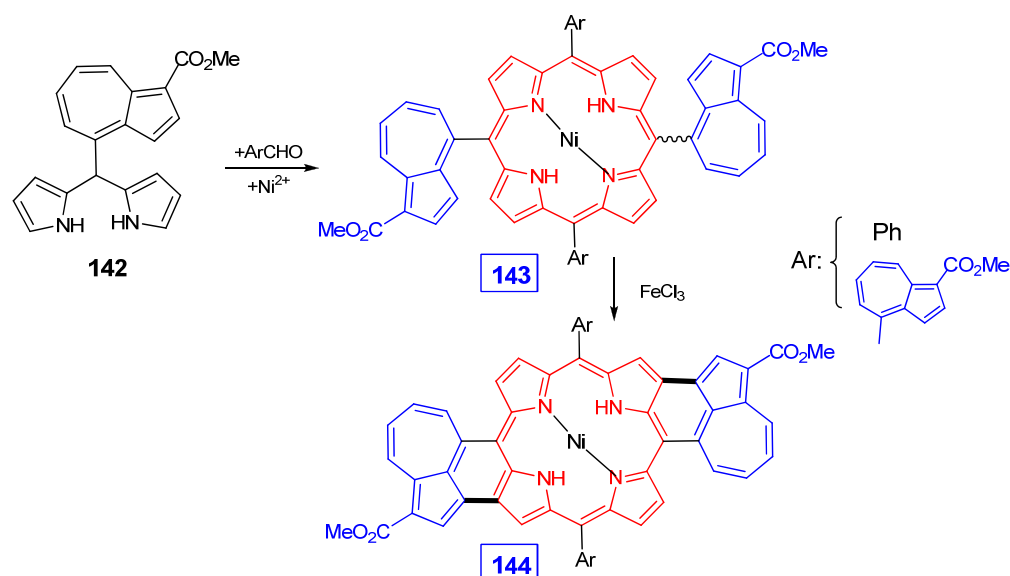
Scheme 26. Calixazulenes.

Asao et al. reported the generation of compound **139** with a 20% yield after successive condensations of 2-methoxyazulene and formaldehyde [64]. Subsequently, Lash succeeded in the synthesis of the all-hydrocarbon calix[4]azulenes **140**a and **140**b by performing the condensation of azulene or 6-*t*Bu azulene with paraformaldehyde in the presence of Florisil® [65,66] with good results. In [62], Georghiou obtained the bulky calixarene **140**c. The spacer methylene in calixarene can be also substituted. Thus, the peculiar ferrocenylmethylene-bridged calix[4]azulene **141** was obtained with moderate yield as the main product with an amount of bis(1-azulenyl)ferrocenylmethane derivative using the reaction of 6-*tert*-butylazulene with ferrocenecarbaldehyde in acetic acid [67]. Products similar to compound **141** with phenyl, *p*-tolyl, and *p*-methoxyphenyl instead of ferrocene [68] were also obtained.

5. The Dancing Circle Group of Azuliporphyrins and Similar Compounds ("Dancing Group" F)
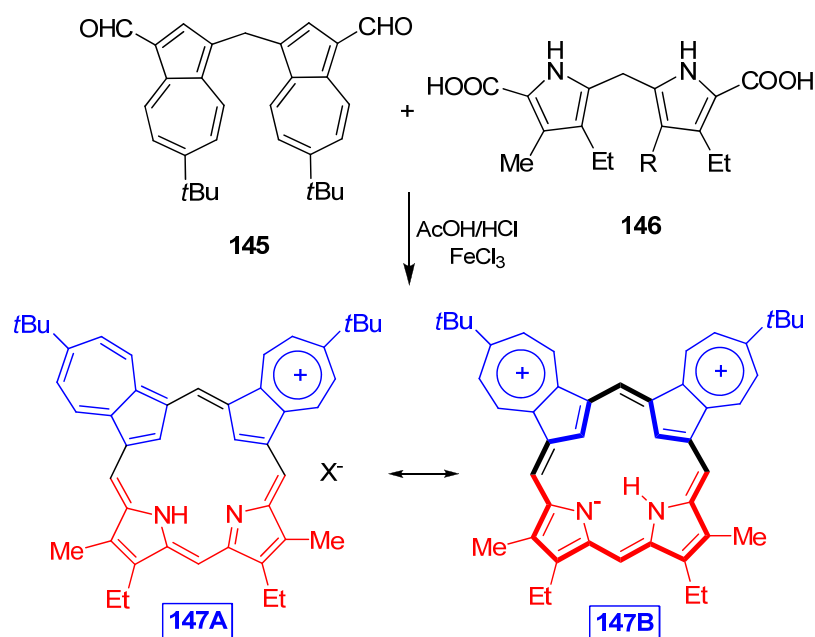
One of the most studied "dancing groups" (Scheme 1) is that with the core porphyrin modified by the replacement of one to all pyrroles with azulene or where the azulene moieties were substituted at the methylene groups of porphyrin. As a result, the number and complexity of products that can be obtained are very high. The reviews and articles that have appeared in this field are impressive. Therefore, here, the data of only a few aspects, especially those related to the synthesis of these products, are covered for information purposes.

Regarding the aim to investigate the extensively conjugated porphyrin with promising two-photon absorption (TPA), compound **143** (both atropisomers) was synthesized starting from dipyrrolmethane **142** (Scheme 26). The two oxidative rings closing (under the Scholl conditions) in intermediate **143** toward the target product Ni^{2+}–5,15-bis(4-azulenyl)porphyrin **144** was due to the electron-rich position 3 in azulene [69]. Interestingly, complex **144** has a symmetric *anti* structure. When the Ar in Scheme 27 was also 1-methoxycarbonylazulene, the same sequence was used to form a very large conjugated quadruply azulene-fused porphyrin. Kurotobi realized a compound with porphyrin that was core-substituted with four 6-azulenyl moieties at the methylene groups using the Ziegler–Natta procedure for the building azulene moieties from the corresponding pyridine [70].
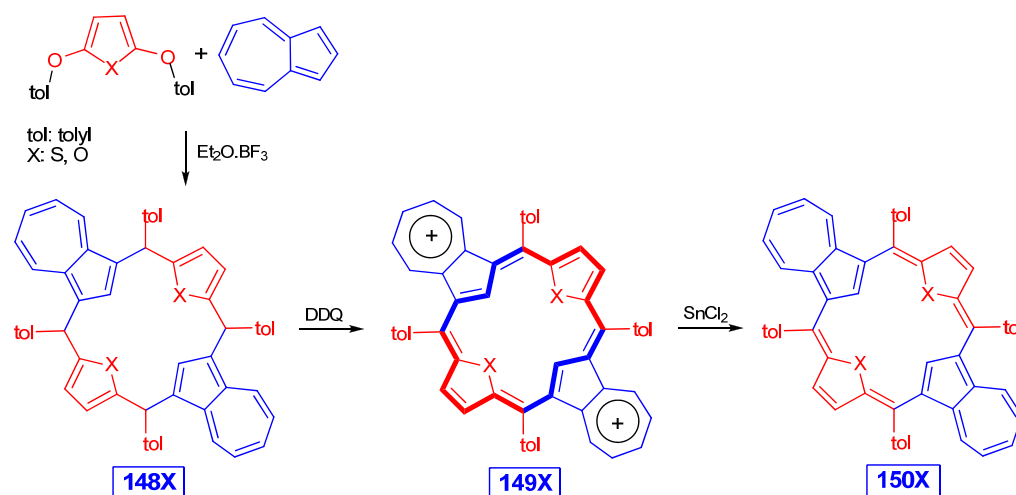
Scheme 27. Synthesis and closing of Ni^{2+}–5,15-bis(4-azulenyl)porphyrin.

The intermediate aromatic properties of azuliporphyrins result in special reactivity and physical properties, for example, strange spectroscopic behavior. The possibility to achieve highly extended π-electron conjugation over pyrroles and azulenes incorporated into the porphyrin skeleton has been of interest to researchers. A careful investigation into the structure of azuliporphyrine with one or two azulenes in the porphyrin ring, based mainly on spectral results, was carried out by Lash et al. [71,72]. Thus, two azulenes were inserted into the porphyrin ring in the *adj* position, namely, side by side. The *adj* isomer **147** was achieved, as described in Scheme 28, by coupling the dialdehyde **145** with dipyrrylmethane **146** and the subsequent oxidation of the formed intermediate with FeCl3 in the presence of HCl or HBr. The zwitterionic canonic structure **147B** leads to the 18π-porphyrinoid macrocyclic aromaticity and tropylium configuration of a seven-membered ring of azulene with remarkable physico-chemical consequences.

Scheme 28. Synthesis of azuliporphyrin.

Finally, other peculiar molecules with extended π-electron conjugation, namely, hybrid thiophene- or furan-azulene macrocycles, are briefly discussed. Latos-Grazynski and co-workers synthesized dithiadiazuliporphyrin (**150S**) with a remarkable 91% yield using the Rothemund-type condensation described in Scheme 29 [73], and when the thiophene ring was replaced by furan, the compound **150**O was produced [74]. Unlike the azulipyridines discussed above, the arrangement of the two azulenes in the min ring is *anti.* The oxidation of condensation intermediate **148** generates the dication **149** with an exceptional structure possessing an extended π-electron conjugation, together with two tropylium cations. The spectral consequences and other properties influenced by the structure of compounds **149** and **150**, as well as the potential for applications in optoelectronics, electrochromic, and molecular conductivity, were discussed in detail in the mentioned articles.

Scheme 29. Synthesis of dioxadiazuliporphyrin and dithiadiazuliporphyrin.

6. Instead of Conclusions

The article was designed out of love for the chemistry of azulene and its derivatives. It does not propose a systematic treatment of a particular topic but tries to cover several areas of this vast chemistry. To avoid "academic rigidity," a less common way of presenting the results belonging to the author and other researchers was preferred, namely, the introduction of azulenes as dancers in a series of dancing groups. In such groups, the connecting position of azulenes can be identical or different, and between azulenes, a spacer can be introduced, leading to an impressive number of possible molecules. Several azulene moieties can form a linear oligomer or a polymer, and the involvement of azulene moieties in nonlinear molecules, such as crown ethers (compounds **C**), azulenophane (compounds **D1** and **D2**), calixazulenes (compounds **E**), or azuliporphyrins (compounds **F**) and similar derivatives (compounds **G**), was intensely studied. Therefore, only some aspects were covered in this review, which were mainly related to the obtaining of azulene compounds and less to their characterization or physico-chemical properties. The review is addressed less to those skilled in azulene chemistry but instead mainly to researchers who want to know something about this fascinating field or maybe even to approach it.

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