

Synthesis and properties of [1,6']biazulenyl compounds

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Abstract

The synthesis of a new biazulenyl system, which contains azulene moieties coupled in 1- and 6-position is reported. The structure of the isolated compounds, as well as the calculated dihedral angle between the planes of the coupled moieties, has been correlated with the recorded spectra.

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1. Introduction

The importance of azulenes as building blocks for design of molecular devices,¹ as well as the peculiarities of compounds that contain two coupled azulenes, has stimulated the interest on synthesis, characterization, and properties of biazulenyl derivatives. The neighborhood of the two azulenyl moieties and the coupling positions strongly influence the charge distribution on the entire molecule and, as a consequence, the properties of the resulting compound.

Two main routes are used for generating biazulenyl derivatives, namely the coupling between two azulene derivatives and the annulation process. The coupling reaction is accomplished by Ullmann condensation,^{2,3} electrochemical,⁴ oxidative,⁵ or photochemical⁶ dimerization, palladium catalyzed intermolecular arylation of unfunctionalized azulene,⁷ Stille cross-coupling reaction of the azulene organotin reagents,⁸ and Miyaura–Suzuki cross-coupling reaction of azulene-1-yl boronate compounds with iodoazulene derivative.^{9,10} The annulation of cyclopentadiene, following the Ziegler–Hafner procedure, has also been reported for the synthesis of several biazulenyl compounds.¹¹

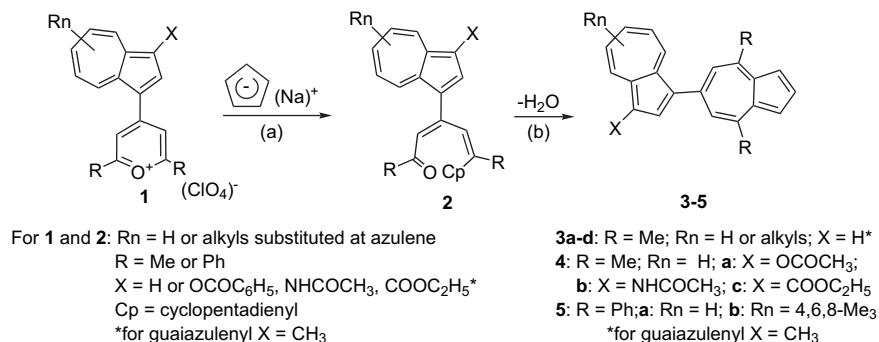
Whereas the synthesis of symmetrical biazulenyl derivatives, coupled in 1,^{2–6} 2,^{2,8,9} 4,^{3,10,12} 5¹¹ and 6^{3,8,11} positions is fairly easy, some problems were encountered while generating unsymmetrical biazulenyls. Preparation of [2,6']^{2,8} and [4,6']³ biazulenyls is accomplished by palladium catalyzed reaction, Miyaura–Suzuki or Stille cross-coupling reactions, and Ullmann condensation. In the case of unsymmetrical biazulenyl systems, when the coupling positions of azulenyl moieties possess very different electron charge, the synthesis pathway is more difficult. Thus, both [1,2']^{2,7} and [1,4']¹⁰ biazulenyl compounds were obtained either in a mixture with other biazulenyl derivatives or in very reduced yields. Although interesting and valuable properties are predictable for [1,6']biazulenyl system, to our knowledge, the syntheses of this type of compounds have not yet been reported.¹³ Therefore, our research goal, reported in this paper, was the synthesis of [1,6']biazulenyl derivatives and the study of some of their properties.

2. Synthesis of [1,6']biazulenyls

The high yields obtained in our previous reported synthesis of 4-(azulene-1-yl) pyranilium salts¹⁴ have suggested us to use these compounds as building blocks for generating [1,6']biazulenyl derivatives. Therefore, the synthesis strategy of this biazulenyl system follows the elegant Hafner-annulation of sodium

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Scheme 1.

cyclopentadienide with pyranilium salts,¹⁵ as described in Scheme 1.

In a typical reaction, the pyranilium salt (0.3 mmol) in THF and sodium cyclopentadienide (0.6 mmol) were vigorously stirred at room temperature for 2 h under inert atmosphere. After this time, an additional quantity of sodium cyclopentadienide (0.3 mmol) has been added and the reaction was continued for 1.5 h in the same conditions. After dilution with water and extraction with dichloromethane (CH₂Cl₂), the resulting residue was chromatographed on alumina (*n*-pentane–CH₂Cl₂ as eluent). Table 1 summarizes the yields of the obtained compounds.

As showed in Table 1, the 2,6-dimethyl-pyranilium salts are more reactive than the corresponding 2,6-diphenyl substituted derivatives. Starting from **1** (R=Me) the biazulenyls were isolated in around 50% yield when the 4-position was occupied by azulene-1-yl or alkyl substituted azulene-1-yl groups, excepting the case of guaiazulenyl derivative. For 4-guaiazulenyl-pyranilium salt, the coupling product, **3c**, is unstable and after several hours an amount of tar was observed in its solution. A severe decrease of the reaction yields was observed in the case of pyranilium salts with electron donating substituents at C3 position of the azulenyl moiety, for instance compound **1** (X=NHAc or OCOPh). The low yields can be attributed to the difficult seven-membered ring closure in the intermediate (step b)¹⁶ and also to the reactivity of the mentioned functional groups with sodium cyclopentadienide. The same type of interaction between sodium salt and CO₂C₂H₅ group lowered the yield during the synthesis of **4c**. The low

yields obtained starting from 2,6-diphenyl-pyranilium salts compared with the corresponding 2,6-dimethyl salts can be also explained by the reduced cyclization capacity of the intermediates, which polymerize in time.

3. Structure and properties of the obtained compounds

HOMO calculation¹⁷ has shown that higher π electron density of the parent azulene is localized on the five-membered ring. This explains the presence of dipole moment and the electrophilic reactivity of the 1(3)-position. For the azulenues bounded in positions with different electronic density, the extension of π electron system onto biazulenyl molecule is favored as compared with the biazulenyls, which are coupled in positions with similar electronic density. Therefore, if one assumes that the biazulenyls have a planar structure, by coupling the energy gap between HOMO and LUMO for the first compounds is conserved or even diminished as compared with the later ones. From these rather simplified arguments, for [1,6'], [1,4'] or [1,2']biazulenyls, an increase of the molecular polarizability is expected and, therefore, a bathochromic effect should be induced.

The deviation from the coplanarity of coupled azulenues, due to steric factors, modifies the conjugation between the π electron systems of the two moieties, depending on the value of dihedral angle, α . This fact has remarkable consequences, mainly for the electronic spectra of biazulenyl compounds. Several considerations regarding the influence of the steric factor on the electronic spectra of symmetrically coupled biazulenyls, evaluated on the basis of molecular models, have been already reported by Hünig and Ort.¹⁸ The bathochromic shift of B band,¹⁹ as well as the increase of its intensity, was observed in the case of [1,1'] and [2,2']biazulenyl compounds as compared to the parent azulene. This was interpreted as being determined by the favorable conjugation of the π electrons of azulenues due to their relative coplanarity. At the same time, the similar wavelengths of B band for azulene and [4,4']biazulenyl compounds can be considered as a consequence of high deviation from coplanarity in the latter, which does not allow the π electrons conjugation.

Taking into account all these informations, we have attempted to correlate the B band position in the recorded electronic

Table 1
Synthesis of [1,6']biazulenyls

Compound		R	Rn	X	η (%)
3	a	CH ₃	H	H	49
	b		4,6,8-(CH ₃) ₃	H	52
	c		3,8-(CH ₃) ₂ ,5- ⁱ Pr	—	17.7
	d		2- ⁱ Bu, 6-CH ₃	H	53
4	a		H	OCOC ₆ H ₅	Traces ^a
	b		H	NHCOCH ₃	14
	c		6-CH ₃	COOC ₂ H ₅	22.6
5	a	C ₆ H ₅	H	H	14.7
	b		4,6,8-(CH ₃) ₃	H	29

^a Detectable as molecular peak by MS spectrometry recorded on the reaction mixture. No further characterization was performed.

Table 2

The calculated dihedral angles and the recorded B band in UV–vis spectra (in methanol or CH₂Cl₂)^a of several biazulenyls^{2,3} compared to the azulene and [1,6']biazulenyl, **3a**

	Biazulenyls						3a [1,6']	AzH
	[2,2']	[1,1']	[6,6']	[4,4']	[2,6']	[1,2']		
α (°)	~1	44/42.5 ^b	58	74/73.4 ^b	31/31.4 ^{b,21}	40/38	50	—
$\lambda_{\max}$ (log ϵ)	433 (4.87), 407 (4.63)	384 (4.19)	381 (4.23)	333 (3.78), 344 (3.83) ^c	418 (4.01), 410 (4.55) ^d	461 (4.27), 441 (4.26)	414 (3.56)	340 (3.63)

^a Hunig and Ort reported similar values in both solvents.

^b Calculated by MM2 procedure.²⁰

^c Shoulder at 357 nm.³

^d Shoulder at 448 nm.²

spectra of the biazulenyl compounds with the values of the dihedral angle α . Therefore, we have calculated the values of α for several biazulenyls that are coupled in different positions using MOPAC 7.0 package and AM1 approach. The resulted values, shown in Table 2, are in agreement with those recently reported by Dias²⁰ when MM2 program has been used.

As shown in Table 2, the decrease of α value determines a bathochromic shift in the series of symmetrical biazulenyl [4,4'], [6,6'], [1,1'], [2,2']. The position of B band in the UV spectra of [2,6']biazulenyls is placed between those of [2,2'] and [1,1']biazulenyls, in accordance with the sequence of α values for these compounds.

The coupling of azulenes in positions 1 and 6 (or 2) produces an important bathochromic effect of the B band despite the relatively high angle α . For these compounds the wavelength of B band surpasses even the wavelength values observed in the case of [1,1'] or [2,6']biazulenyls, which have smaller α values. We suppose that for [1,6'] or [1,2']biazulenyl isomers, the energy band gap between the HOMO and LUMO is less affected by the deviation from coplanarity than in the case of the other isomers. In the case of [1,6']biazulenyl compound **3d** the bulk *tert* butyl group in 2-position of azulenyl moiety, significantly increases the α angle. This leads to a dramatic hypsochromic effect accompanied by a concomitant stretch of the coupling bond. Table 3 shows that a 24° deviation of α value, resulted passing from structure **3a** to **3d**,

Table 3

The calculated dihedral angles, bridging bond length, and the band B wavelengths in the recorded UV–vis spectra of [1,6']biazulenyls

	3a	3d	5a
α (°)	50	74	52
Bond length (Å)	1.460	1.480	1.468
$\lambda_{\max}$ (log ϵ)	414 (3.56)	340 (3.63)	347 (4.06), 395 (3.45)

Table 4

¹H-chemical shifts for [1,6']biazulenyls

Compound	Protons, δ (ppm)						
	5-H and 7-H ^a	3-H/1'(3')-H	6-H	2-H/2'-H	4-H	8-H	5' (7')-H
Azulene	7.18	7.40	7.60	7.90	8.36	8.36	—
3a	7.21, 7.22	7.46/7.44	7.65	8.12/7.74	8.40	8.59	7.47
3d	6.85, 7.03	7.28/7.44	—	—	7.53	8.12	7.44
5a	7.21, 7.24	7.43/7.16	7.60	8.14 ^b	8.37	8.70	7.54

^a Indefinite signal attribution.

^b 7.68–7.71 (m, 5H, 2'-H, 2''-H, 6''-H).

causes a hypsochromic shift of 74 nm and a 0.020 Å lengthening of the coupling bond. It is to note that identical B band wavelengths are recorded for **3d** and azulene. As expected, an intense bathochromic effect is observed for the diphenyl substituted biazulenyls, **5a** and **5b**, determined by the extension of aromatic system.

The molecular geometry of the [1,6']biazulenyls can be also monitored by ¹H NMR spectroscopy (Table 4). The identical chemical shifts for 5'-H and 7'-H for all compounds indicate that, regardless of the azulenes substituents, the free rotation around the coupling bond remains possible. The 1,6'-coupling (for example, in the case of compound **3a**) has a little influence on the chemical shifts of the protons at C3, C4, C5 and C7, which are far away from the coupling positions. At the same time, the protons at C2 and C8, located in the peripheral zone of the azulene-6'-yl group, are downfield shifted due to the anisotropic magnetic effect of the above-mentioned group. The large increase of the angle α in compound **3d** leads to a significant modification in the orientation of magnetic field and lowers the conjugation between the two bounded azulenes. That can explain the shielding of all protons of azulene-1-yl moiety for this compound (some contribution can be also attributed to the inductive effect of alkyl substituents).

Replacement of methyl groups at C2' and C8' by phenyls in azulene-6'-yl moiety (**3a** toward **5a**) insignificantly modifies the chemical shifts of the protons belonging to azulene-1-yl group, proving that this group is not influenced by the change of inductive and electromeric effects or of the magnetic field anisotropy due to this replacement.

In conclusion, the attractive structure and the interesting properties of the [1,6']biazulenyl system justify the proposed protocol for synthesizing these new compounds, in spite of the moderate yields of the annulation reaction. The relative

position of the two coupled azulenes in biazulenyls, the nature of their substituents, and the dihedral angle between their planes strongly influence the electronic spectra of the biazulenyl compounds and in some extent the NMR spectra. The energetic band gap between HOMO and LUMO of the biazulenyls, which are coupled in positions with similar electronic demand is strongly influenced by the variation of the angle α . However, the deviation from coplanarity in the case of azulenes that are coupled in positions with different electronic charges, i.e., [1,2'] or [1,6']biazulenyls, might have a significant smaller influence on the energy difference between HOMO and LUMO. This can explain the bathochromic effect on the B band observed for these two compounds, in spite of their rather high angle α . A study regarding the molecular orbitals of biazulenyls is in progress in our research group.

Our attention is also focused on the generation of other [1,6']biazulenyl derivatives, namely those obtained starting from substituted cyclopentadienide salts and on the investigation of the chemical properties of the synthesized compounds.

4. Experimental part

4.1. General

Melting points are uncorrected: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin–Elmer CHN 240B. UV spectra in methanol: Varian Cary 100 spectrophotometer. ^1H and ^{13}C NMR: Bruker Avance DRX4 (^1H : 400 MHz, ^{13}C : 100.62 MHz) and Gemini 300 (^1H : 300 MHz, ^{13}C : 75.47 MHz), J values are given in hertz, TMS was used as internal standard in CDCl_3 as solvent, at room temperature; COSY and HETCOR correlation experiments were used for the structure assignment. Mass spectra: Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI or APCI. IR spectra: Bruker Vertex 70. For the column chromatography alumina [II–III, 70–230 mesh ASTM] was used. CH_2Cl_2 was distilled over CaH_2 . The pyranilium salts substituted in 4-position with azulene were obtained as described in our previous paper.¹⁴

4.2. General procedure

Pyranilium salt (0.3 mmol) was partly dissolved in dry THF (10 mL) under inert atmosphere. Sodium cyclopentadienide in THF (0.6 mmol, 0.30 mL of 2 M solution) was added and the resulted mixture was vigorously stirred for 2 h at room temperature. Then, one additional equivalent of sodium cyclopentadienide (0.3 mmol) has been added and the reaction continued in the same conditions for 1.5 h. The resulting solution was diluted with water and extracted several times with CH_2Cl_2 . The organic layers were dried over Na_2SO_4 and finally evaporated under vacuum to remove the solvent. The crude product was purified by chromatography on alumina with n -pentane– CH_2Cl_2 =20/1 as eluent to give green compounds. For the compound **4a** the eluent was ethyl acetate– n -pentane=1/1 and for compound **4b**, CH_2Cl_2 – n -pentane=2/1.

4.3. Product characterization

4.3.1. 4',8'-Dimethyl-[1,6']biazulenyl (**3a**)

Green crystals, mp 123–125 °C. UV–vis (MeOH): λ_{max} (log ϵ) 244 (3.90), 276 (3.85), 297 (3.82), 309 (3.83), 414 (3.56), 560 (2.05) nm. ^1H NMR (400 MHz, CDCl_3): δ 2.98 (s, 6H, 4'-Me, 8'-Me), 7.21 (t, 1H, 5-H or 7-H, J =10.0 Hz), 7.22 (t, 1H, 7-H or 5-H, J =10.0 Hz), 7.44 (d, 2H, 1'-H, 3'-H, J =3.6 Hz), 7.46 (d, 1H, 3-H, J =4.0 Hz), 7.47 (s, 2H, 5'-H, 7'-H), 7.65 (t, 1H, 6-H, J =9.8 Hz), 7.74 (t, 1H, 2'-H, J =3.8 Hz), 8.12 (d, 1H, 2-H, J =3.6 Hz), 8.40 (d, 1H, 4-H, J =9.6 Hz), 8.59 (d, 1H, 8-H, J =10.0 Hz) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): δ 25.39 (Me-4', Me-8'), 116.23 (C-1', C-3'), 117.64 (C-3), 123.80 (C-5 or C-7), 124.15 (C-7 or C-5), 128.49 (C-5', C-7'), 133.17 (C-2'), 135.86 (Cq), 135.91 (C-8), 136.07 (Cq), 137.72 (C-4), 138.09 (C-2), 138.50 (C-6), 142.23 (Cq), 144.80 (Cq), 145.39 (Cq) ppm. ESI-MS (positive mode): m/z (%)=283.1 (100) [$\text{M}+1$]. Elemental Analysis Calcd for $\text{C}_{22}\text{H}_{18}$ [282 g/mol]: C 93.58%, H 6.42%; Found: C 93.50%, H 6.48%. IR (solid): ν_{max} 2919s, 2852s, 1558m, 1528m, 1455m, 1387m, 1208w, 889w, 861w, 782w, 730m (cm^{-1}).

4.3.2. 4,6,8,4',8'-Pentamethyl-[1,6']biazulenyl (**3b**)

Green crystals, mp 153–154 °C; UV–vis (MeOH): λ_{max} (log ϵ) 215 (4.00), 245 (3.84), 283 (3.78), 299 (3.93), 421 (3.19), 546 (1.90) nm. ^1H NMR (400 MHz, CDCl_3): δ 2.48 (s, 3H, 4-Me), 2.64 (s, 3H, 6-Me), 2.94 (s, 6H, 4'-Me, 8'-Me), 2.95 (s, 3H, 8-Me), 7.02 (s, 1H, 7-H), 7.11 (s, 1H, 5-H), 7.35 (s, 2H, 5'-H, 7'-H), 7.39 (d, 1H, 3-H, J =4.4 Hz), 7.45 (d, 2H, 1'-H, 3'-H, J =4.0 Hz), 7.69 (d, 1H, 2-H, J =4.0 Hz), 7.74 (t, 1H, 2'-H, J =4.0 Hz) ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 25.19 (Me-4', Me-8'), 25.58 (Me-8), 28.50 (Me-6), 29.46 (Me-4), 114.97 (C-3), 116.12 (C-1', C-3'), 127.54 (C-5), 129.19 (C-5', C-7'), 129.23 (C-7), 131.28 (Cq), 132.87 (C-2'), 136.07 (Cq), 136.41 (C-2), 136.84 (Cq), 137.46 (Cq), 144.56 (Cq), 146.23 (Cq), 146.59 (Cq), 147.61 (Cq), 149.64 (Cq) ppm. ESI-MS (positive mode): m/z (%)=325.1 (100) [$\text{M}+1$]. Elemental Analysis Calcd for $\text{C}_{25}\text{H}_{24}$ [324 g/mol]: C 92.54%, H 7.46%; Found: C 92.49%, H 7.48%. IR (solid): ν_{max} 3096w, 3062w, 2919s, 2851s, 1561m, 1529m, 1417m, 1376m, 1325w, 1262w, 1207w, 1182w, 1064w, 1016w, 866w, 837w, 778w, 738m (cm^{-1}).

4.3.3. 5-Isopropyl-3,8,4',8'-tetramethyl-[1,6']biazulenyl (**3c**)

Green crystals, mp 158–160 °C. UV–vis (MeOH): λ_{max} (log ϵ) 215 (4.01), 245 (4.00), 286 (4.04), 292 (4.04), 434 (3.37), 546 (2.42) nm. ^1H NMR (400 MHz, CDCl_3): δ 1.40 (d, 6H, Me_2CH , J =6.8 Hz), 2.45 (s, 3H, 8-Me), 2.71 (s, 3H, 3-Me), 2.93 (s, 6H, 4'-Me, 8'-Me), 3.11 (heptet, 1H, Me_2CH), 6.97 (d, 1H, 7-H, J =10.8 Hz), 7.32 (s, 2H, 5'-H, 7'-H), 7.42 (dd, 1H, 6-H, J =11.2, 2.0 Hz), 7.43 (d, 2H, 1'-H, 3'-H, J =3.6 Hz), 7.68 (s, 1H, 2-H), 7.73 (t, 1H, 2'-H, J =4.0 Hz), 8.25 (d, 1H, 4-H, J =2 Hz) ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 12.87 (Me-3), 24.66 (Me_2CH), 25.19 (Me-4', Me-8'), 28.39 (Me-8), 37.91 (Me_2CH), 116.10 (C-1', C-3'), 124.32 (Cq), 127.35 (C-7), 129.36 (C-5', C-7'),

131.76 (Cq), 132.81 (C-2'), 133.51 (Cq), 134.13 (C-4), 135.16 (C-6), 136.01 (Cq), 138.11 (Cq), 140.14 (C-2), 140.54 (Cq), 144.37 (Cq), 146.21 (Cq), 148.99 (Cq) ppm. ESI-MS (positive mode): m/z (%) = 353.1 (100) [M+1]. Elemental Analysis Calcd for $C_{27}H_{28}$ [352 g/mol]: C 91.99%, H 8.01%; Found: C 91.90, H 8.00%. IR (solid): $\nu_{\max}$ 3093w, 3059w, 2957s, 2924s, 2869s, 1566s, 1422s, 1369m, 1326w, 1247w, 1206w, 1076m, 1020m, 866w, 749m (cm^{-1}).

4.3.4. 2-*tert* Butyl-6,4',8'-trimethyl-[1,6']biazulenyl (3d)

Green crystals, mp 122–124 °C. UV–vis (MeOH): $\lambda_{\max}$ (log ϵ) 206 (4.33), 243 (4.56), 277 (4.78), 295 (4.92), 347 (4.06), 395 (3.45), 558 (2.58) nm. 1H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, t -Bu), 2.54 (s, 3H, 6-Me), 2.88 (s, 6H, 4'-Me, 8'-Me), 6.85 (d, 1H, 5-H, J =10.2 Hz), 7.03 (d, 1H, 7-H, J =9.6 Hz), 7.26 (s, 2H, 5'-H, 7'-H), 7.28 (s, 1H, 3-H), 7.44 (d, 2H, 1'-H, 3'-H, J =3.8 Hz), 7.53 (d, 1H, 4-H, J =10.1 Hz), 7.76 (t, 1H, 2'-H, J =3.8 Hz), 8.12 (d, 1H, 8-H, J =9.9 Hz) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.97 (Me-4', Me-8'), 27.79 (Me-6), 32.06 (Me- t -Bu), 34.90 (Cq- t -Bu), 114.90 (C-3), 116.12 (C-1', C-3'), 124.44 (C-5, C-7), 130.25 (C-5', C-7'), 133.43 (C-2'), 133.62, 133.71 (C-8), 134.70 (C-4), 134.71 (Cq), 136.78 (Cq), 137.33 (Cq), 137.75 (Cq), 144.51 (Cq), 147.62 (Cq) ppm. ESI-MS (positive mode): m/z (%) = 353 (100) [M+1]. Elemental Analysis Calcd for $C_{27}H_{28}$ [352 g/mol]: C 91.99%, H 8.01%; Found: C 91.93%, H 8.03%. IR (solid): $\nu_{\max}$ 3095w, 3070w, 3010w, 2953m, 2919m, 2853m, 1563s, 1479m, 1420s, 1314w, 1242w, 1206m, 1069w, 1008w, 862w, 812m, 746s (cm^{-1}).

4.3.5. *N*-(4',8'-Dimethyl-[1,6']biazulenyl-3-yl)-*N*-methyl-formamide (4b)

Green crystals, mp 140–142 °C. UV–vis (MeOH): $\lambda_{\max}$ (log ϵ) 245 (4.42), 284 (4.53), 314 (4.38), 424 (3.97); 559 (2.70) nm. 1H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H, $COCH_3$), 2.78 (s, 6H, 4'-Me, 8'-Me), 6.88 (t, 1H, 5-H or 7-H, J =9.6 Hz), 6.91 (t, 1H, 7-H or 5-H, J =9.5 Hz), 7.25 (s, 2H, 5'-H, 7'-H), 7.27 (d, 2H, 1'-H, 3'-H, J =4.0 Hz), 7.39 (t, 1H, 6-H, J =9.7 Hz), 7.58 (t, 1H, 2'-H, J =3.9 Hz), 7.94 (d, 1H, 4-H, J =10.1 Hz), 8.29 (s, 1H, 2-H), 8.28 (d, 1H, 8-H, J =9.1 Hz) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 25.65 (Me-4', Me-8'), 30.08 ($COCH_3$), 116.58 (C-1', C-3'), 122.48 (C-5 or 7), 124.28 (C-7 or 5), 128.62 (Cq), 128.88 (C-5', C-7'), 132.23 (C-2'), 132.51 (C-2), 133.55 (Cq), 133.63 (C-8), 134.10 (Cq), 136.99 (C-4), 139.62 (C-6), 145.65 (Cq), 155.34 (Cq), 155.55 (Cq), 168.79 (Cq) ppm. ESI-MS (positive mode): m/z (%) = 340 (100) [M+1]. Elemental Analysis Calcd for $C_{24}H_{21}NO$ [339 g/mol]: C 84.92%, H 6.24%, N 4.13%; Found: C 84.85%, H 6.28%, N 4.15%. IR (solid): $\nu_{\max}$ 2958s, 2927s, 2872m, 2858s, 1729 ($\nu_{C=O}$), 1567w, 1461m, 1380w, 1270m, 1170w, 1122m, 1072m, 1039w, 960w, 868w, 739w, 704w (cm^{-1}).

4.3.6. 6,4',8'-Trimethyl-[1,6']biazulenyl-3-carboxylic acid ethyl ester (4c)

Green crystals, mp 134–135 °C. UV–vis (MeOH): $\lambda_{\max}$ (log ϵ) 206 (4.36), 242 (4.50), 286 (4.60), 309 (4.57), 397

(4.11), 542 (2.86) nm. 1H NMR (300 MHz, $CDCl_3$): δ 1.47 (t, 3H, CH_2CH_3 , J =7.1 Hz), 2.72 (s, 3H, 6-Me), 2.97 (s, 6H, 4'-Me, 8'-Me), 4.4 (q, 2H, CH_2CH_3 , J =7.2 Hz), 7.21 (dd, 1H, 5-H, J =9.1, 1.1 Hz), 7.25 (s, 2H, 5'-H, 7'-H), 7.29 (d, 2H, 1'-H, 3'-H, J =3.9 Hz), 7.33 (dd, 1H, 7-H, J =9.1, 1.2 Hz), 7.76 (t, 1H, 2'-H, J =3.9 Hz), 8.45 (s, 1H, 2-H), 8.53 (d, 1H, 8-H, J =10.2 Hz) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 15.01 (CH_3CH_2), 25.67 (Me-4', Me-8'), 28.35 (Me-6), 60.23 (CH_2CH_3), 116.37 (Cq), 116.77 (C-1', C-3'), 128.59 (C-5', C-7'), 129.49 (C-5), 129.56 (C-7), 133.77 (C-2'), 135.16 (Cq), 136.57 (C-2), 136.65 (C-8), 138.08 (C-4), 139.38 (Cq), 139.62 (Cq), 140.74 (Cq), 144.25 (Cq), 145.82 (Cq), 152.75 (Cq), 165.81 (CO) ppm. ESI-MS (positive mode): m/z (%) = 369 (60) [M+1], 320 (100). Elemental Analysis Calcd for $C_{26}H_{24}O_2$ [368 g/mol]: C 84.75%, H 6.56%; Found: C 84.72%, H 6.57%. IR (solid): $\nu_{\max}$ 3095s, 3064s, 2918s, 2851s, 1690 ($\nu_{C=O}$), 1565m, 1511w, 1431s, 1382m, 1202w, 1152w, 1102w, 1070m, 1038m, 858w, 816w, 765w, 733w (cm^{-1}).

4.3.7. 4',8'-Diphenyl-[1,6']biazulenyl (5a)

Green oil. UV–vis (MeOH): $\lambda_{\max}$ (log ϵ) 202 (4.61), 236 (4.60), 287sh (4.58), 305 (4.63), 435 (4.21), 558 (2.89) nm. 1H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 2H, 1'-H, 3'-H, J =4.0 Hz), 7.21 (t, 1H, 7-H, J =9.6 Hz), 7.24 (t, 1H, 5-H, J =9.6 Hz), 7.43 (d, 1H, 3-H, J =4.0 Hz), 7.46–7.53 (m, 6H, 3''-H, 4''-H, 5''-H), 7.54 (s, 2H, 5'-H, 7'-H), 7.60 (t, 1H, 6-H, J =9.6 Hz), 7.68–7.71 (m, 5H, 2'-H, 2''-H, 6''-H), 8.14 (d, 1H, 2-H, J =3.8 Hz), 8.37 (d, 1H, 4-H, J =9.2 Hz), 8.70 (d, 1H, 8-H, J =9.6 Hz) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): 117.82 (C-3), 120.08 (C-1', C-3'), 123.99 (C-7), 124.42 (C-5), 124.83 (C-6), 127.76 (C-5', C-7'), 127.90 (C-4''), 128.10 (C-3'', C-5''), 128.38 (C-2'), 129.26 (C-2'', C-6''), 134.68 (Cq), 135.84 (C-8), 137.72 (C-4), 138.24 (Cq), 138.56 (C-2), 142.44 (Cq), 144.55 (Cq), 145.00 (Cq), 149.68 (Cq) ppm. ESI-MS (positive mode): m/z (%) = 407 (100%) [M+1]. Elemental Analysis Calcd for $C_{32}H_{22}$ [406 g/mol]: C 94.55%, H 5.45%; Found: C 94.43%, H 5.49%. IR (solid): $\nu_{\max}$ 3059w, 3028w, 2958s, 2927s, 2858m, 1560m, 1538m, 1495m, 1459m, 1447m, 1436m, 1418m, 1339w, 1276m, 1126w, 1075w, 1029w, 771m, 743m, 702m (cm^{-1}).

4.3.8. 4,6,8-Trimethyl-4',8'-diphenyl-[1,6']biazulenyl (5b)

Green crystals, mp 184–185 °C. UV–vis (MeOH): $\lambda_{\max}$ (log ϵ) 202 (4.40), 244 (4.43), 287sh (4.41), 300 (4.53), 441 (3.82), 555 (2.80) nm. 1H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 6H, 4'-Me, 6'-Me), 2.58 (s, 3H, 8-Me), 2.62 (s, 3H, 6-Me), 2.87 (s, 3H, 4-Me), 6.99 (s, 1H, 7-H), 7.04 (s, 1H, 5-H), 7.15 (d, 2H, 1'-H, 3'-H, J =3.98 Hz), 7.32 (d, 1H, 3-H, J =4.12 Hz), 7.37 (s, 2H, 5'-H, 7'-H), 7.37–7.48 (m, 6H, 3''-H, 4''-H, 5''-H), 7.62–7.65 (m, 4H, 2''-H, 6''-H), 7.67 (d, 1H, 2-H, J =4.12 Hz), 7.70 (t, 1H, 2'-H, J =4.23 Hz) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): 25.88 (Me-4', Me-8'), 28.79 (Me-4), 29.73 (Me-6), 30.66 (Me-8), 115.43 (CH), 120.25 (CH), 125.87 (CH), 127.89 (CH), 128.12 (CH), 128.35 (CH), 128.93 (CH), 129.56 (CH), 129.73 (Cq), 131.86 (Cq), 134.79 (CH), 136.95 (CH), 137.09 (Cq), 137.38 (Cq), 138.06 (Cq), 144.77 (Cq), 146.50

(Cq), 146.86 (Cq), 147.71 (Cq), 149.12 (Cq), 150.08 (Cq) ppm. ESI-MS (positive mode): m/z (%)=449 (100) [M+1]. Elemental Analysis Calcd for C₃₅H₂₈ [448 g/mol]: C 93.71%, H 6.29%; Found: C 93.90%, H 6.09%. IR (solid): $\nu_{\max}$ 2958w, 2929s, 2854s, 1558m, 1540w, 1458m, 1377w, 1271w, 1179w, 1073w, 1027w, 768w, 745w, 700w (cm⁻¹).

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