

2,13-Diaza[5]helicene: synthesis, theoretical calculations and spectroscopic properties

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This paper is dedicated to Professor Nicolò Vivona for his 70th birthday

Abstract

An easy approach to the synthesis of azahelicenes is based on the photochemical cyclisation of symmetrically or asymmetrically 1,2-aryl-substituted double bonds. In the synthesis of 2,13-diaza[5]helicene, irradiation of 9-(2-pyridin-4-yl-vinyl)-benzo[*h*]isoquinoline yielded 2,9-diaza-dibenzo[*a,h*]anthracene together with the desired helicene, and the ratio of the two products depends on the solvent. In this paper we suggest that the ratio between the two products should not be ascribed to different transitions induced by the solvent but to different populations of the two *Z* conformers

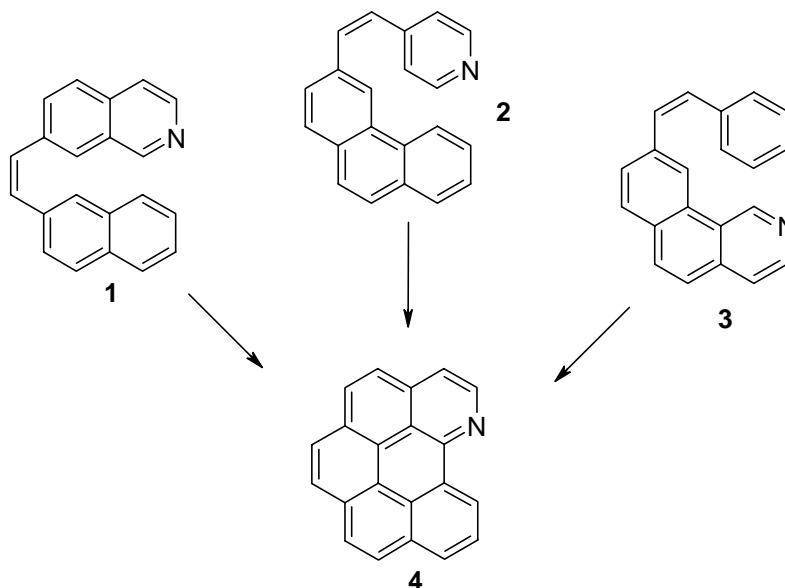
Keywords: 2,13-Diaza[5]helicene, 2,9-diaza-dibenzo[*a,h*]anthracene, solvent polarity, photochemical ring closure, theoretical calculations, NMR

Introduction

In the series of aza[5]helicenes, the ones containing one or two nitrogen atoms are particularly attractive in view of forming complexes with metal ions.¹ In the past, we reported the synthesis

of a certain number of monoaza^{2,3} and diazahelicenes³, generally utilizing a photochemical approach.

However, for the synthesis of 2-aza[5]helicene a non photochemical approach was employed.² The reason was that the photochemical ring closure of all possible precursors to this molecule, namely 7-(2-naphthalen-2-yl-vinyl)-isoquinoline (**1**), 4-(2-phenanthren-3-yl-vinyl)-pyridine (**2**) and 9-styryl-benzo[*h*]isoquinoline (**3**) all brought exclusively to the corresponding perylene (**4**) (Scheme 1).

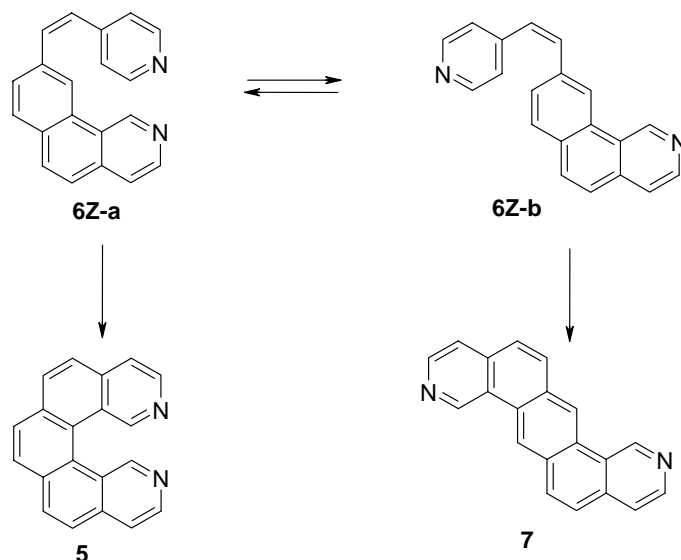


Scheme 1

Theoretical calculations suggested that the perylene formation is, by far, the favored photochemical closure.² Similar difficulties were anticipated in designing the photochemical synthesis of 2,13-diaza[5]helicene, and for this reason a non-photochemical approach was devised at first, but the overall yield was extremely low,⁴ so as to call for a different approach.

Results and Discussion

Interestingly, ab initio calculations performed on **6** showed similarities with other calculations referred to those monoazahelicenes which can be obtained by irradiation so as to predict the possibility to obtain **5** photochemically. Furthermore, these calculations suggested also that irradiation would yield not only the helicene, but also 2,9-diaza-dibenzo[*a,h*]anthracene (**7**) from a competing pathway (Scheme 2).



Scheme 2

As described in ref. 2 we considered a “free valence” atomic index, analogous to the one introduced in the context of the Hückel model.^{5a,b} We examined the two possible conformations **6Z-a** and **6Z-b**: the first one with the pyridine ring oriented inwards, in a geometry close to (**5**), the second one with the pyridine ring oriented outwards, similar to (**7**) (Scheme 2).

The presence of these two conformations in solution was confirmed by NMR. Compound **6Z** was examined in both benzene- d_6 and methanol- d_4 . Steady state nuclear Overhauser enhancement (NOE) experiments were carried out in order to assess the conformational preferences. NOE difference spectra pointed out that, in both cases, conformers **6Z-a** and **6Z-b** are present in solution and in fast exchange on the NMR time-scale. The results are summarized in Table 1.

Table 1. NOE data of compound **6Z**. In parentheses the conformer consistent with observed NOE (legend: a = **6Z-a**; b = **6Z-b**, see Scheme 2)

Irradiated	Observed NOE % (conf.)	Observed NOE % (conf.)
	benzene- d_6	methanol- d_4
H10	H2,2'(py) 2.8% (a)	H2,2'(py) 1.2% (a)
	H11(vinylic) 3.5% (b)	H11(vinylic) 5.1% (b)
H2,2'(py)	H10 1.0% (a)	H10 1.2% (a)
	H8 1.0% (b)	H8 1.3% (b)
H11(vinylic)	H10 2.2% (a)	H10 2.9% (a)
	H8 0.4% (b)	H8 1.9% (b)

Unfortunately, the expected stabilization of a single conformation by varying the solvent polarity was not observed. As a matter of fact, in both solvents, the two conformations depicted

in Scheme 1 are appreciably populated. Cautious use of quantitative NOE % data seems to suggest that **6Z-a** is slightly stabilized with respect to **6Z-b** in methanol-d₄, and the vice versa in benzene-d₆.

The two conformers may be considered precursors of **5** and **7** respectively (Scheme 2). Excited states of these two conformers have been optimized in the CIS framework with 6-31G basis set; this permits a comparison with data obtained previously;⁵ we used the GAUSSIAN03 package.⁶ In all cases the conformers are distorted, the pyridine ring and the phenanthridine system lying in two different planes: the dihedral angles responsible for non-planarity are torsions about the simple CC bonds at the ground state (optimization B3LYP/6-31G), and the torsion about the double bond at the first excited state (CIS).

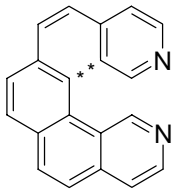
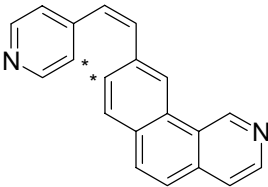
In our previous paper,² in order to find an explanation to the different outputs of the experiments for the production of helicenes, the value of an atomic index had been calculated by means of the Natural Bond Orbital program⁷ included in the package GAUSSIAN03. We defined an atomic quantity F_A that mimics the “free valence” atomic index introduced in the past in the context of the Hückel model.^{4a,b}

$$F_A = V_A - \sum_{B \neq A} b^{(w)}_{AB}$$

where V_A is the atomic valence returned by the NBO program as the sum of occupation numbers of the valence orbitals (as opposed to core orbitals) of atom A , $b^{(w)}_{AB}$ is the Wiberg bond index^{7a,b} of atoms A and B , and the sum is made over all the atoms B other than A . The above index has been calculated in the first excited state for the atoms of interest (F_A^*).

In Table 2 we report the values of the differences $\Delta F^* = |F_X^* - F_Y^*|$, X and Y being the carbon atoms possibly involved in the closure.

Table 2. Difference of the bond indexes for the atoms involved in the ring formation

	6Z-a		6Z-b	
$\Delta F^* = F_X^* - F_Y^* $	0,114		0,081	

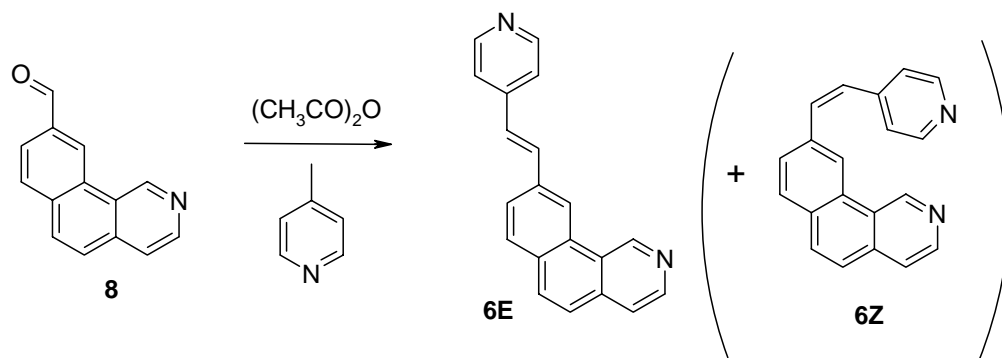
It has been reported for monoaza-compounds (see for example ref. 5b and references cited therein) that the closure yielding the helicene is favoured with respect to the formation of the anthracene, and that this fact corresponds to the highest values for ΔF^* . In the case of the precursor of 2-aza[5]helicene instead, the highest value for ΔF^* regards the two carbons

corresponding to the closure giving (**4**) and in fact no trace of the 2-aza[5]helicene was detected in the photochemical reaction. In the case of monoaza-compounds it was found that all the conformers similar to **6Z-b** have lower values for ΔF^* , minor than half the value obtained for the conformers of type **6Z-a**; actually, for monoaza compounds no dibenzoanthracene byproducts were detected, despite the fact that the energies for **b** conformers are slightly lower than the energies for **a**.

In the case of 2,13-diaza[5]helicene here considered, the same kind of calculations gave a lower value of ΔF^* in case of conformer **6Z-b** than for conformer **6Z-a**; however the difference is small: this suggests that (**5**) may be obtained together with (**7**) through two competing pathways.

The theoretical work needed to understand the photochemical process is beyond the scope of this work; what reported is just a preliminary indication to guide the choice of the chemical route but only a real experiment can say the last word. Remarkably, however, the example reported here is another instance of good correlation between calculation and experiment in the same framework. For these reasons, photochemical synthesis of **5** was attempted, starting from (**6**); this latter could be obtained through several alternative synthetic routes.

(a) the direct condensation of **8** with 4-methyl pyridine to give the precursor **6-E**, (Scheme 3)



Scheme 3

(b) The reaction of **8** with pyridin-4-yl-methyl-triphenylphosphonium bromide. In this case a mixture of the Z (80%) and E (20%) isomers of **6** is obtained

(c) The Mizoroki-Heck coupling; considering that 4-vinyl pyridine is a common product, and the counterpart, 9-Br-Benzo[h]isoquinoline is easy to synthesise,⁹ this could be considered a viable alternative approach, but our attempts to obtain (**6**) following this procedure^{10a-d} gave very low yields.

Once **6** is obtained, a first photolysis experiment was run in ethyl acetate and, as expected, both products **5** and **7** were obtained in a 6.8 to 1 ratio. However, in order to raise the yield of **2**, the reaction was conducted in different solvents to explore the possibility of exploiting polarity effects. The results are shown in Figure 1.

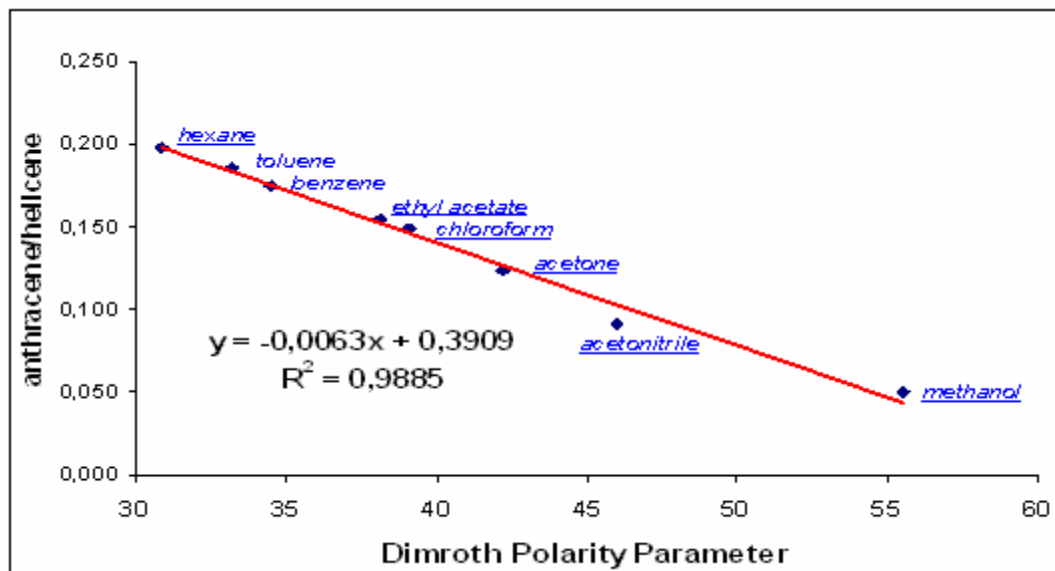


Figure 1. Correlation between the Dimroth solvent polarity parameter and the ratio anthracene/phenanthrene.

A simple explanation of the trend evidenced in Figure 1 may be that in non polar solvents **6** interacts preferentially with the solvent molecules, stabilizing to a certain extent the open conformation **6Z-b** that would bring to **7**, while in polar solvents an intramolecular interaction stabilizing **6Z-a** must be preferred, eventually giving **5** as main product.

Since the mechanism of formation is likely the same for both products, the absence of changes due to solvent polarity in the energy of the transitions¹⁰ were excluded by analysis of the absorption and the emission spectra of the Z isomer in some of the used solvents.

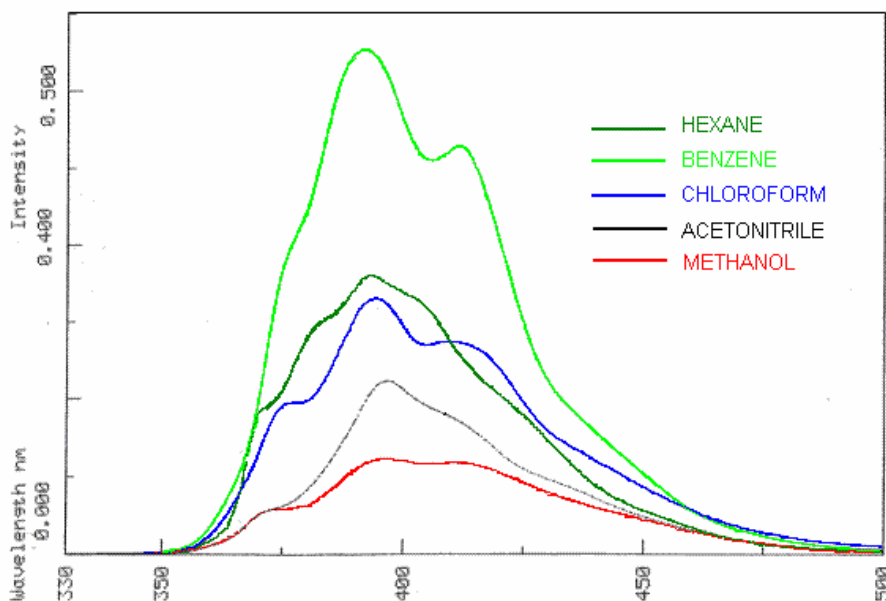


Figure 2. Emission spectra of **6-Z** in selected solvents.

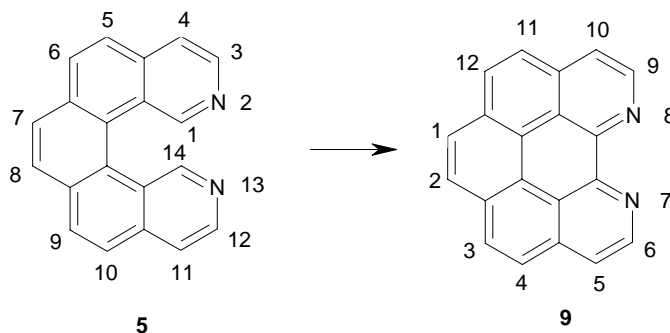
The shift of maxima in the different solvents is very limited both for absorption and emission spectra, though some differences are observed in the intensity of emitted light (Figure 2). Indeed, calculations allow to predict a huge difference in the dipole moment of the **6Z-a** and **6Z-b** conformers both in the ground state and in the excited state, as can be seen in Table 3

Table 3. Calculated dipole moments in Debye for the ground and excited states of **6Z-a** and **6Z-b** conformers

	6Z-a	6Z-b
Ground state	5.14	2.06
Excited state	5.67	2.66

It can be also remarked that ring closure to give **5** is by far the preferred pathway compared to the one giving **7**. This means that the excited state of **6Z-b** may live long enough to choose between two deactivation channels: light emission or ring closure. Oppositely, ring closure is strongly favoured for **6Z-a** and the channel of deactivation through emission is inactive in this case. Consequently, the fluorescence emissions are indicative of the population of the two conformers **6Z-a** and **6Z-b**. The only exception to this trend is observed in benzene, where the relative emission is much higher than in the other cases and for which we see no simple explanation.

Finally, prolonged irradiation brings to the formation of 7,8-diaza-benzo[*ghi*]perylene (**9**), but differently from the cases of (**2**) and (**3**) in Scheme 1, here the products derives from reaction of the photochemically excited helicene (Scheme 4). In the Scheme, the numbering used in the discussion of the NMR spectra is included.



Scheme 4

Conclusions

Differently from the photochemical synthesis of the other mono- and diaza[5]helicenes, irradiation of 9-(2-pyridin-4-yl-vinyl)-benzo[*h*]isoquinoline gives rise to the formation not only of helicene **5**, but also of the competing product **7**; their ratio depends on the polarity of the used

solvent. A theoretical explanation of the observed trends is proposed. The perylene **9** is formed only for prolonged irradiation, at variance with the behaviour described for the related compound **4**.

Experimental Section

Ab initio calculations. GAUSSIAN03 package was used.⁶ Ground state has been optimized at B3LYP/6-31G level; optimization on excited states has been done using single-excitation configuration interaction, CIS, with the same basis set. Natural Bond Orbital program⁷ included in the package GAUSSIAN03 has been used to calculate atom indices.

General Procedures. All solvents were distilled and dried before use. 4-picoline, 4-vinylpyridine, triphenylphosphine, acetic anhydride, are commercial products and were used without further purification. Irradiations were carried out on a Rayonet RPR-100 photochemical reactor equipped with 16 interchangeable lamps irradiating either at 254, 313, or 365 nm as well as in the visible range, dissolving the substance in the appropriate solvent in quartz or Pyrex vessels, depending on the used wavelength.

9-[2-Pyridin-4-yl-vinyl]-benzo[*h*]isoquinoline (**6**)

Method A. 4-methylpyridine (0.16 mL, 1.6 mmol) was refluxed with aldehyde **8** (0.070 g, 0.33 mmol) in acetic anhydride (15mL) for 48h. After cooling at room temperature, a 2M aqueous solution of NaOH was carefully added on cooling with an external ice bath, and the solution extracted not less than 4 times with 10mL portions of CH₂Cl₂. After drying and solvent evaporation, the residue (0.186 g) was chromatographed on silica gel (Ethyl acetate and then Ethyl acetate: ethanol 4:1) recovering **8** (0.028 g) and obtaining **6-E** as a yellow solid in 27% yield (0.040 g).

Method B. In a flask containing a mixture of the aldehyde **8** (1 mmol) and MeONa (0.065 g, 1.2 mmol), pyridin-4-ylmethyl-triphenylphosphonium bromide (1 mmol) in methanol (15 mL), was dropped during 3 h under stirring and boiling. After cooling, water was added, and the solution extracted not less than 4 times with a large volume of CH₂Cl₂. After drying and solvent evaporation, the residue was chromatographed on silica gel (Ethyl acetate and then Ethyl acetate/ethanol 4:1) obtaining **6** as a deliquescent brownish yellow solid in (0.240 g, 85% yield) (20% E isomer 80% Z isomer)

Method C. In a flask containing 4-bromobenzaldehyde (6.4 mmol) dissolved in 3 mL of Ac₂O and kept at 140°C a solution of 4-picolin (4 mmol) dissolved in 1 mL of Ac₂O is added dropwise during a few minutes; the mixture is kept at 140°C during 4 h, then a 2M aqueous HCl solution is added and the mixture extracted once with 20 mL of CH₂Cl₂. The aqueous layer is made basic with 2M aqueous NaOH solution and the mixture extracted 4 times with overall 50 mL of CH₂Cl₂. After drying, TLC analysis (AcOEt/hexane 2:1) shows mostly 4-bromobenzaldehyde in

the acidic extract and two spots attributed to Z- and E-4-[2-(4-bromo-phenyl)-vinyl]-pyridine products by comparison with authentic samples. Furthermore, GC-MS of the solution shows two peaks with m/z 260. The solution is evacuated and the residue weighed 230 mg (22% yield). This residue is then dissolved in AcOEt, transferred in a Pyrex vessel and photolyzed at 366 nm for 1h30'. The reaction is followed by TLC and stopped when the reagents are no longer present. 0.35 mmol of the crude product (9-bromobenzo[h]isoquinoline) is then dissolved in 5 mL of dimethylacetamide; to this solution 1 mmol of 4-vinylpyridine, 1 mmol of sodium acetate and 1% of bis(triphenylphosphine)palladium (II) dichloride were added and the mixture stirred at 140°C during 48 h. At the end, the mixture is cooled, diluted with 2M aqueous NaOH and extracted 4 times with overall 50 mL of CH_2Cl_2 . GC-MS analysis reveals traces (< 5%) of both **6Z** and **6E** and a large amount of the starting material.

Compound characterization. NMR spectra were performed on Bruker Avance 500 spectrometer operating at proton resonance frequency of 500 MHz. The products were dissolved in suitable deuterated solvent and tetramethylsilane (TMS) was added as internal reference. GC-MS analyses were obtained from an Agilent GC 6890 series gas-chromatograph equipped with a MS 5973N mass spectrometer detector. Electrospray mass spectra (ESI-MS) were acquired on a Bruker Esquire 3000+ by infusion of suitable solution directly in the ESI source at the rate of 4 $\mu\text{L}/\text{min}$. The ATR FT-IR spectra were recorded on a Avatar 370-Thermo or on a Bruker Tensor 27. UV-vis spectra were run on a Thermo Evolution 500 spectrometer with 10^{-5} M solutions in the appropriate solvent. Fluorescence spectra were run on a Jasco 770 spectrofluorimeter utilizing the same solutions used for the UV-vis spectra. HPLC analyses were run on a Perkin-Elmer series 200 instrument using a Zorbax Eclipse XDB-C18 analytical column 4,6 x 150 mm, 5- μm . Solvent $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 8/2, flow rate 1.0 mL/min. Elemental analyses were run at the Dipartimento di Chimica, Materiali e Ingegneria Chimica del Politecnico di Milano.

6Z. Oil, ESI-MS: 283 $[\text{M}+\text{H}]^+$; IR: 2963 ; 2924 ; 1706 ; 1590 ; 1437 ; 1401 ; 1331 ; 1238; 1062; UV (CH_3OH) λ (log ϵ) 205 (4.24), 249 (4.24), 321(4.01). ^1H NMR (500 MHz, CD_3OD , 25°C, δ , ppm): 9.57, s, 1H, H1; 8.57, br. s, 1H, H10; 8.44, 1H, d, $J = 5.6$ Hz, H3; 8.23, m, 2H, H1(py); 7.84, 1H, d, $J = 8.9$ Hz, H5 or H6; 7.71, d, 1H, $J = 8.5$ Hz, H7; 7.70, 1H, dd, $J = 5.5, 1.2$ Hz, H4; 7.61, 1H, d, $J = 8.9$ Hz, H6 or H5; 7.36, 1H, dd, $J = 8.5, 1.8$ Hz, H8; 7.13, 2H, m, H2(py); 7.01, 1H, d, $J = 12.3$ Hz, H11; 6.54, 1H, d, $J = 12.3$ Hz, H12.

Anal. calc. for $\text{C}_{20}\text{H}_{14}\text{N}_2$: C 85.08, H 5.00, N 9.92; found C 84.76, H 5.01, N 9.90.

6E. Mp 184-186°C; ESI-MS: 283 $[\text{M}+\text{H}]^+$; IR: 3022; 1613; 1589; 1410; 1239; 1213; 969; 848; UV (CH_3OH) λ (log ϵ): 205 (4.11), 239(4.24), 270(4.01), 332 (4.23). Anal. calc. for $\text{C}_{20}\text{H}_{14}\text{N}_2$: C 85.08, H 5.00, N 9.92; found C 84.59, H 4.99, N 9.95.

2,13-Diaza[5]helicene (5).¹² The irradiation was carried out in methanol (0.030 g in 200mL) for 50' at 365 nm. At the end of irradiation, the solvent was removed under vacuum, and the residue (0.030 g) was chromatographed on silica gel (CH_3CN : 2-propanol : ethanol 6:3:1) recovering **6** (0.020 g) and obtaining **5** (0.008 g, yield 27%, yield on converted base 80%) as a light yellow

solid, mp 255-260°C. Mass (m/e) 279, 253; ESI-MS: 281 [M+H]⁺; IR: 2960; 2921; 2852; 1613; 1542; 1401; 1260; 1228; 1029; 858; 801, UV (CH₃OH) λ (log ϵ): 203(4.49), 225(4.60), 266(4.24), 307 (4.26). ¹H NMR (500 MHz, CDCl₃, 25°C, δ , ppm): 9.92, s, 1H, H1; 8.60, d, 1H, J = 5.4 Hz, H3; 8.08, 1H, d, J = 8.7 Hz, H5 or H6; 7.97, s, 1H, H7; 7.91, 1H, d, J = 8.7 Hz, H6 or H5; 7.76, d, 1H, J = 5.4 Hz, H4. Anal. calc. for C₂₀H₁₂N₂: C 85.69, H 4.32, N 9.99; found C 85.84, H 4.30, N 9.97.

2,9-Diaza-dibenzo[*a,h*]anthracene (7). The irradiation was carried out in hexane (0.030 g in 200 mL) for 1h30' at 360 nm. At the end of the irradiation, the solvent was removed under vacuum, and the residue (0.029 g) was chromatographed on silica gel (CH₃CN : 2-propanol : ethanol 6:3:1) recovering **6** (0.002 g) and obtaining **5** as a light yellow solid (0.021 g in 70% yield); and **7** as a brown-red solid (0.004 g 15% yield).

7: mp 242-250°C, mass (m/e) 280, 253; ESI-MS: 281 [M+H]⁺; IR: 2945; 2836; 1648; 1541; 1507; 1456; 1418; 1015; UV (CH₃OH) λ (log ϵ) 216(4.58), 266(4.27), 308(4.10), 335 (4.11); ¹H NMR (500 MHz, CDCl₃, 25°C, δ , ppm): 9.04, s, 1H, H1; 8.48, d, 1H J = 5.7 Hz, H3; 7.85, 1H, d, J = 8.50 Hz, H5 or H6; 7.77, s, 1H, H7; 7.76 1H, d, J = 8.50 Hz, H6 or H5; 7.70, d, 1H J = 5.7 Hz, H4. Anal. calc. for C₂₀H₁₂N₂: C 85.69, H 4.32, N 9.99; found C 85.75, H 4.30, N 9.96.

7,8-Diazabenz[ghi]perylene (9). The irradiation was carried out in hexane (0.030 g in 200mL) for 3h30' at 365 nm. At the end of irradiation, the solvent was removed under vacuum, and the residue (0.029 g) was chromatographed on silica gel (CH₃CN : 2-propanol : ethanol 6:3:1) obtaining **7** in (0.004 g, 13% yield) and **9** as a dark orange solid (0.023 g, 77% yield)

9: mp 226-234°C, mass (m/e) 278; ESI-MS: 279 [M+H]⁺; IR: 2966 ; 2922 ; 1613 ; 1594; 1559; 1429 ; 1400 ; 1368 ; 1331 ; 1089; 856; UV (CH₃OH) (log ϵ) 203(4.61), 252 (4.46), 287(4.36), 299(4.23), 353(3.62), 373(3.74), 393(73.86) ¹H NMR (500 MHz, CD₃COCD₃, 25°C, δ , ppm): 9.40, d, 1H, J = 5.2 Hz, H6; 8.66, s, 1H, H2; 8.56, 1H, d, J = 8.8 Hz, H3 or H4; 8.34, d, 1H, J = 5.2 Hz, H5; 8.33, 1H, d, J = 8.8 Hz, H4 or H3. Anal. calc. for C₂₀H₁₀N₂: C 86.31, H 3.62, N 10.07; found C 86.00, H 3.63, N 10.02.

Photolysis in different solvents. 10 mL of 2.0 10⁻⁴ M solution of **6** in the appropriate solvent was irradiated for 1 h at 363 nm. At the end of irradiation, the solvent was removed under vacuum, and the residue was dissolved in 10 mL of CH₃OH and analysed via HPLC as described above. Peak areas were corrected for the different absorbances.

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12. Compound **5** was already reported in ref 4. Despite the fact that the NMR spectra show the same number of signals and the same multiplicity and they appear quite clean, the chemical shifts are different. Moreover there is a strong difference in the melting points. Due to the small amount of material obtained at that time, it was not possible to make a comparison between the former product and the one obtained now. We have no explanation for this difference.