



Synthesis, computational, and photophysical characterization of diaza-embedded [4]helicenes and pseudo[4]helicenes and their pyridinium and viologen homologues



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ARTICLE INFO

Article history:

Received 10 December 2016

Accepted 15 December 2016

Available online 18 December 2016

Keywords:

Helicenes

Viologens

Photophysics

Computational chemistry

Racemization barriers

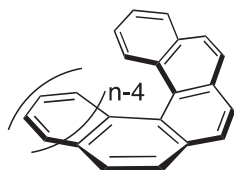
ABSTRACT

Synthesis of three [4]heli-viologens and their helical precursors, and two “pseudo-[4]helicenes” and their alkylated derivatives, which have potential device and catalysis applications, are reported. Their structures and racemization barriers have been explored with the B3LYP/6-311+G(2d,p), M06-2X/6-311+G(2d,p), and M11/6-311+G(2d,p) computational models. The photophysical properties of the helicenes and pseudo-helicenes and their alkylated derivatives have been measured. Unusual singlet-triplet energy gaps, ΔE_{ST} , were measured and discussed for the charged alkylation products.

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1. Introduction

[n]Helicenes are a polyaromatic hydrocarbon family consisting of an array of ortho-fused aromatic rings, **1**.¹ Their best known, and most intriguing, characteristic is their chiral helical topology which is first expressed in [4]helicene, **1** ($n = 4$). This topology leads to extraordinary physical and chiroptical properties that have been used to advantage by many workers during construction of novel molecular switches, sensing devices, and catalysts, and for the synthesis of supramolecular, opto-electronic, and non-linear materials.^{2,3}



1 ($n = 4, 5, 6, \dots$)

Recently considerable effort has been expended to synthesize and study heterohelicenes formed by embedding a heteroatom into

one or more of the aromatic rings of the carbocyclic [n]helicene or by replacing one or more of the aromatic rings with a hetero-aromatic ring (e.g. furan, or thiophene).^{4–6} The impetus for these studies was the observations of interesting, useful, and enhanced properties induced by heteroatom substitution.⁷ In 2006 the complete series of seven mono-aza[5]helicenes was reported.⁸ This remarkable achievement came 98 years after the first report of the synthesis of [5]helicene.⁹ The wait, however, was worth it, since access to the entire series has provided compelling evidence that judicious placement of the nitrogen atom within the helical framework can be used to selectively modulate a wide-range of physicochemical properties of these valuable molecules.¹⁰ Building on this exceptional body of work, we recently embedded viologen functionality into [5]helicene.¹¹ (Fig. 1) Addition of the viologen functional group simultaneously generates a redox addressable helicene,^{12–14} a fluorescent organic salt,^{15,16} and a potent photo-acid,^{17–19} which are properties of current interest for device construction.

We now extend these efforts, to embed nitrogen functionality into the helical scaffolds of [4]helicene, **1** ($n = 4$), and benzo[b]-[4]helicene and report the synthesis and photophysical behavior of three diaza[4]helicenes, **2a–c**, two planar diaza-[b]benzo[4]helicenes (pseudo-helicenes), **3a** and **3b**, three heli-[4]viologens, **2j–l**, and two pyridinium derivatives, **3d** and **3g**. We also describe computational studies of these compounds and several derivatives of **2** and **3** to provide insight into their structural features and

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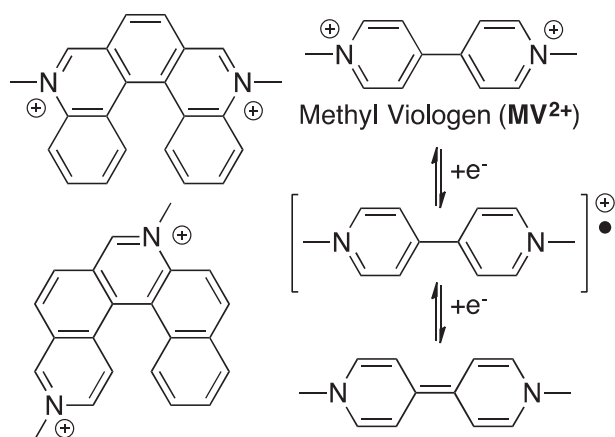
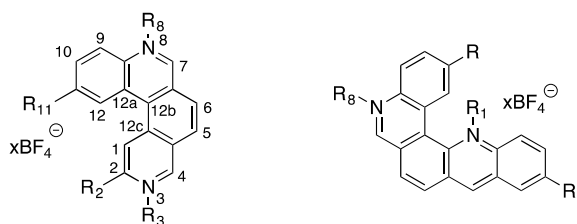


Fig. 1. Helical Viologens and their Redox States.

racemization barriers.



2					3				
	R ₂	R ₃	R ₈	R ₁₁	X	R	R ₁	R ₈	X
a	H	●●	●●	H	0	a	H	●●	0
b	H	●●	●●	CH ₃	0	b	CH ₃	●●	0
c	CH ₃	●●	●●	H	0	c	H	●●	1
d	H	CH ₃	●●	H	1	d	H	CH ₃	1
e	H	●●	CH ₃	H	1	e	H	●●	1
f	CH ₃	CH ₃	●●	H	1	f	CH ₃	●●	1
g	CH ₃	●●	CH ₃	H	1	g	CH ₃	●●	1
h	H	CH ₃	●●	CH ₃	1	h	CH ₃	●●	1
i	H	●●	CH ₃	CH ₃	1	i	H	CH ₃	2
j	H	CH ₃	CH ₃	H	2	j	H	H	2
k	H	CH ₃	CH ₃	CH ₃	2	k	H	CH ₃	2
l	CH ₃	CH ₃	CH ₃	H	2	l	H	H	2
l	CH ₃	CH ₃	CH ₃	H	2	m	CH ₃	CH ₃	2

●●-lone pair

2. Results and discussion

Synthesis. Syntheses of the diaza[4]helicenes (Fig. 2a) and diazabenz[4]helicenes (Fig. 2b) were accomplished in straightforward two-pot procedures and were then alkylated in one additional step to generate their monoalkylated (pyridinium) or dialkylated (viologen) derivatives. The first step in both procedures is the Pd-catalyzed vinylation (Hiyama-Heck reactions) of bromopyridines or bromoquinolines with triethoxyvinylsilane.^{20,21} Both the sequential one-pot two step and the one-step Hiyama-Heck couplings leading to unsymmetrical, **4**, and symmetrical **5** (E)-1,2-diarylethylenes, respectively, occurred in good to excellent yields (65–91%). The photocyclizations to form the helicenes occurred in modest yields and in the case of the (E)-diquinoylethylenes, **5**, to a separable mixture of cyclization products (**3a** and **6** (R = H) or **3b** and **6** (R = CH₃)). The structure of **6** (R = H) was unambiguously assigned by comparison to an authentic sample.¹¹ Despite the low yield of **6** (R = CH₃) and our inability to isolate it pure, we argue that it is 2,13-dimethyl-5,10-diaza[5]helicene based on the analogous

formation of **6** (R = H) in the reaction of **5** (R = H), mechanistic considerations, and a crude proton NMR spectrum. (See Supplementary Material) The ratio [**3b**]/[**6**; R = CH₃] was much greater than [**3a**]/[**6**; R = H] reflecting dramatic steric destabilization of 2,13-dimethyl-5,10-diaza[5]helicene, (**6**; R = CH₃).

The alkylations were conducted with trimethyloxonium tetrafluoroborate, (CH₃)₃OBF₄, and led to the viologens in reactions of the [4]helicenes, **2a**, **2b**, and **2c**, and to pyridinium tetrafluoroborates in the reactions of the benzo[*b*]-1,8-diaza[4]helicenes, **3a** (R = H) and **3b** (R = CH₃). The reactions with diaza-*[b]*benzo[4]helicenes, **3a** (R = H) and **3b** (R = CH₃) but not with the [4]helicenes, **2a**, **2b**, and **2c** required DBU (1,8-diazabicycloundec-7-ene). It is tempting to suggest that adventitious HBF₄ impurity in the (CH₃)₃OBF₄ preferentially protonates the exposed nitrogen rather than the nitrogen in the cove regions of **3a** and **3b** (Scheme 1a). Subsequent alkylation is then directed to the unprotonated sterically inaccessible buried nitrogen in the cove regions and consequently fails. In the case of the [4]helicenes, **2a**, **2b**, and **2c** initial protonation still leaves an exposed nitrogen where alkylation can occur. Rapid loss of the acidic hydrogen from the monoalkylated-protonated [4]helicene, **7**, followed by the second alkylation gives the viologen without the need for DBU (Scheme 1b).

The scenario in Scheme 1 is supported by the observation that addition of triethylamine to the (CH₃)₃OBF₄/**3b** reaction mixture without DBU resulted in an immediate color change from reddish-yellow to yellow consistent with a change in the protonated/deprotonated equilibrium (Scheme 1). The diminished basicity of the cove region nitrogen is also supported by B3LYP and M06-2X calculations using the 6-311+G(2d,p) basis set in CH₃CN that show that **3a** protonated at the cove nitrogen is 3.36 and 3.26 kcal/mol less stable, respectively, than **3a** protonated at the exposed nitrogen. This corresponds to the exposed nitrogen (N₈) being more basic than the less sterically accessible nitrogen (N₁) by 2.4–2.6 pKa units (Scheme 1).

2.1. Structural aspects

Key B3LYP and M06-2X/6-311+G(2d,p) structural features of diaza[4]helicenes, **2a**, **2b**, and **2c**, and their viologen counterparts **2j**, **2k**, and **2l** in the absence of their weakly coordinating BF₄[−] counterions,¹¹ are compared to their carbocyclic analogue [4]helicene, **1** (n = 4) in Table 1. All six compounds adopt a helical structure. The non-planar geometry of **1** (n = 4), and the reliability of our computational methods, are convincingly demonstrated by X-ray crystallography,²² proton²³ and carbon NMR,²⁴ and by PES.²⁵ The dihedral angles, $\Theta_{12,12a,12b,12c}$ and $\Theta_{12a,12b,12c,1}$, that define the cove region decrease along the series [4]helicene > viologens > diaza[4]helicenes (Table 1). These dihedral angles are very similar to the two outer dihedral angles that define the fjord region in the analogues [5]helicene. For example the three B3LYP/6-311+G(2d,p) dihedral angles that define the fjord region in **1** (n = 5) [18.2°, 30.2°, and 18.1°], are larger than in the viologen dimethyl-5,10-diaza[5]helicene viologen [17.0°, 29.8°, 17.0°], which are larger than in 5,10-diaza[5]helicene [16.9°, 27.9°, 16.9°]. The smaller intracove dihedral angles in the diaza[4]helicenes in comparison to the corresponding angle in [4]helicene can be attributed to a slight increase in the d_{1,12} distance (Table 1) in the diaza[4]helicenes that allows the ring system to adopt a more planar geometry with a reduced energetic cost. The increases in $\Theta_{12a,12b,12c,1}$ upon alkylation of **2a**, **2b**, and **2c** to give the viologens are consistent with an energetic preference to decrease the overlap between the two pyridinium rings. However, these B3LYP and M06-2X/6-311+G(2d,p) dihedral angles of 17.6°–17.9° and 18.4°–18.8°, respectively, are substantially smaller than the 40° interpyridinium ring angle adopted in methyl viologen, which is not

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