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# Tuning the redox profile of the 6,6'-biazulenic platform through functionalization along its molecular axis†

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The  $E_{1/2}$  potential associated with reduction of the linearly-functionalized 6,6'-biazulenic scaffold is accurately correlated to the combined  $\sigma_p$  Hammett parameters of the substituents over > 600 mV range. X-ray crystallographic analysis of the 2,2'-dichloro-substituted derivative revealed unexpectedly short C–Cl bond distances, along with other metric changes, suggesting a non-trivial cycloheptafulvalene-like structural contribution.

Originally isolated from plant essential oils in the nineteenth century, azulenic compounds continue to fascinate scientists to this day. The correct structure of the polar azulenic scaffold,  $C_{10}H_8$ , ( $\mu \approx 1.1$  Debye<sup>1</sup>) that features fused five- and seven-membered  $sp^2$ -carbon rings was first recognized by Pfau and Plattner in 1936.<sup>2</sup> The X-ray crystallographic confirmation of azulene's molecular structure was reported 20 years later.<sup>3,4</sup> Azulenic building blocks are attractive for developing  $\pi$ -functional molecules and materials.<sup>5–7</sup> Among the three possible linear biazulenes, 6,6'-biazulene has recently been emerging as a particularly effective oligoazulenic  $\pi$ -linker in the design of molecular electron reservoirs,<sup>8</sup> on-chip microsupercapacitors,<sup>9</sup> quasi-molecular rectifiers,<sup>10</sup> organic and organometallic self-assembled monolayer (SAM) films,<sup>8,11</sup> and organic field-effect transistors.<sup>12</sup> Since the synthesis of 6,6'-biazulene in 1980,<sup>13</sup> access to its derivatives, especially those functionalized along its molecular axis, has been quite limited.<sup>11,14,15</sup>

Given that azulene's highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO) have complementary orbital density distributions, their energies can be varied independently, to a first approximation.<sup>16–18</sup> This is accomplished by considering the position of attachment of a substituent to the azulenic core, as well as its electron withdrawing/donating ability.<sup>19</sup> In this communication, we envisioned a similar approach for tailoring the energetics of the frontier molecular orbitals of the linear 6,6'-biazulenic framework. Indeed, Fig. 1 illustrates the orbital density complementarity between the HOMO and LUMO of 6,6'-biazulene.

Herein, we demonstrate that the redox potential ( $E_{1/2}$ ) of the 6,6'-biazulenic scaffold is accurately predictable based on the Hammett  $\sigma_p$  parameters<sup>20</sup> of the substituents X and X' incorporated along its molecular axis (Fig. 2). To the best of our knowledge, this is the first study unveiling such quantitative redox correlations in the context of azulenic  $\pi$ -systems. In addition, we discuss how dichloro substitution exerts unexpected structural permutations within compound **3a** (X = X' = Cl) in the solid state.

To facilitate synthetic accessibility of 2,2'-functionalized 6,6'-biazulenes, we selected the 1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**1**) as the "parent" platform. Rather than employing a toxic organotin reagent to assemble **1** *via* Stille cross-coupling,<sup>21</sup> our synthesis of this compound involved simple deamination of the biazulenic derivative **2a** (Scheme 1). On the other hand, subjecting **2a** to Sandmeyer chlorination afforded dark purple, nearly black, crystalline

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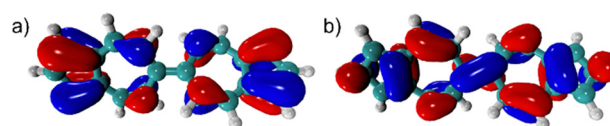


Fig. 1 Highest occupied (a) and lowest unoccupied (b) molecular orbitals (HOMO and LUMO) of 6,6'-biazulene (B3LYP functional and cc-pVDZ basis set).



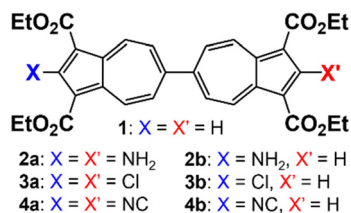
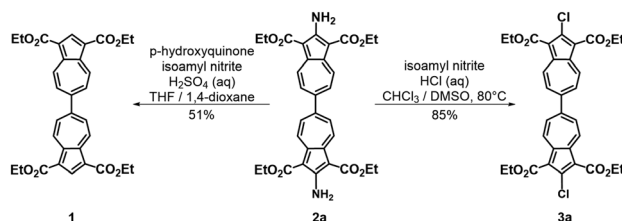


Fig. 2 2,2'-Functionalized 6,6'-biazules considered in this work.



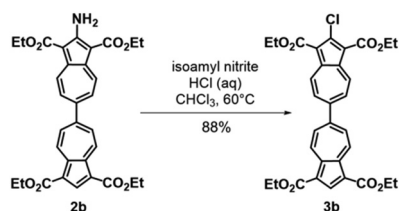
Scheme 1 Syntheses of 1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**1**) and 2,2'-dichloro-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**3a**).

2,2'-dichloro-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**3a**) in an 85% yield (Scheme 1). Thus, **3a** can be prepared from 2-amino-6-bromo-1,3-diethoxycarbonylazulene<sup>22</sup> in two steps with an overall yield of *ca.* 80% (Scheme S1, ESI<sup>†</sup>).<sup>14</sup> In addition to **3a**, we synthesized its unsymmetric congener, 2-chloro-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**3b**), *via* Sandmeyer chlorination of our recently reported 2-amino-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**2b**) (Scheme 2).<sup>8</sup> Both **3a** and **3b** constitute versatile precursors to a variety of 2-, and 2,2'-functionalized 6,6'-biazules.

Given that unsymmetrically functionalized **3b** is a structural hybrid of centrosymmetric **1** and **3a**, it is reasonable that its <sup>1</sup>H NMR spectrum (Fig. S7, ESI<sup>†</sup>) appears as a superposition of the <sup>1</sup>H patterns observed for the latter compounds (Fig. S1 and S2, ESI<sup>†</sup>).

We assigned all resonances in the <sup>13</sup>C NMR spectrum of **3a** *via* synergistic consideration of its HSQC, HMBC, and 1,1-ADEQUATE<sup>23–26</sup> 2-D maps (Fig. S3–S6, ESI<sup>†</sup>). Notably, this is the only unambiguously assigned <sup>13</sup>C NMR profile of any 6,6'-biazulene reported in the literature to date.

Our TD-DFT calculations (Table S4, ESI<sup>†</sup>) corroborate that the lowest energy broad band centered around 500 nm in the electronic absorption spectrum of **3a** (Fig. 3a) corresponds to the HOMO → LUMO and HOMO–1 → LUMO transitions. The broad nature of this band can be attributed, in part, to the range of accessible microstates pertaining to the



Scheme 2 Synthesis of 2-chloro-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene (**3b**).

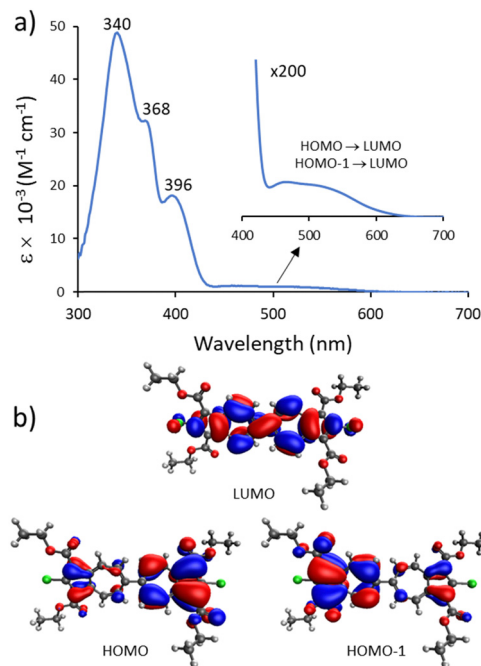


Fig. 3 (a) Electronic absorbance spectrum of **3a** in CH<sub>2</sub>Cl<sub>2</sub> at 22 °C. (b) TD-DFT calculated molecular orbitals of **3a** involved in the S<sub>0</sub> → S<sub>1</sub> transition.

azulene–azulene interplanar angle within **3a** in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>11</sup> While the LUMO of **3a** involves the entire biazulenic core, **3a**'s nearly degenerate HOMO and HOMO–1 are each primarily localized on one of the azulenic units (Fig. 3b).

We have recently shown that 2,2'-functionalized 6,6'-biazules undergo reversible one-step, 2e<sup>−</sup> reduction in CH<sub>2</sub>Cl<sub>2</sub>/<sup>t</sup>Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>−</sup> solutions under the potential inversion regime<sup>27</sup> regardless of whether they feature symmetric or asymmetric substitution along their molecular axis.<sup>8</sup> After recognizing a qualitative relationship between the E<sub>1/2</sub> values associated with the 2e<sup>−</sup> reduction of the 6,6'-biazulenic core and the electron donating/withdrawing characteristics of the 2,2'-substituents, we set out to identify a quantitative approach for tuning the 6,6'-biazulenic redox profile (Fig. S13–S16, ESI<sup>†</sup>). Remarkably, plotting the half-wave redox potential (E<sub>1/2</sub>) against the combined σ<sub>p</sub> Hammett parameters<sup>20</sup> of the substituents X and X' for the seven 6,6'-biazulenic derivatives listed in Fig. 2 revealed a nearly perfect linear correlation over > 600 mV range (Fig. 4 and Table S5, ESI<sup>†</sup>). While attempts to correlate molecular redox potentials with the Hammett parameters of functional groups have been reported in the past for benzenoid organic/organometallic and ferrocene-based compounds,<sup>28–31</sup> this is the first example of invoking such a relationship for a cohort of azulenic derivatives. Notably, a similar trend (E<sub>p,c</sub> vs. σ<sub>p</sub>) holds for the family of 2-substituted 1,3-diethoxycarbonyl azulenes shown in Fig. 5 and Table S6 (ESI<sup>†</sup>). However, the 1e<sup>−</sup> reduction of the latter compounds is invariably irreversible (Fig. S17–S20, ESI<sup>†</sup>).<sup>11</sup> Coupling any pair of 2-substituted azulenes to form the corresponding 6,6'-biazulene leads to full reversibility of the reduction, with the biazulenic E<sub>p,c</sub>



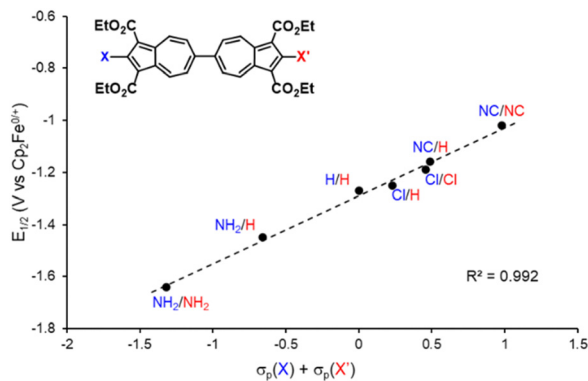


Fig. 4 A plot of the  $2e^-$  reduction potential ( $E_{1/2}$ ) for 2,2'-functionalized 6,6'-biazulenenes vs. the combined  $\sigma_p$  Hammett parameters of the substituents X and X'.

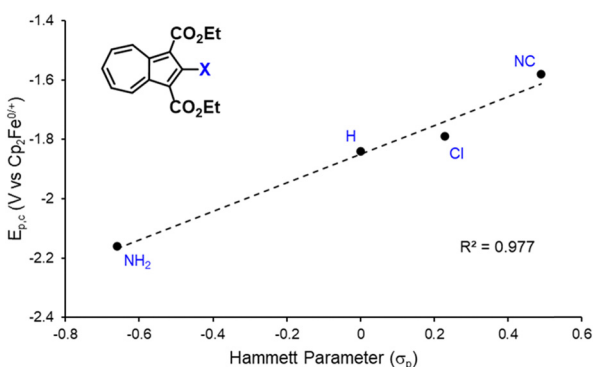


Fig. 5 A plot of the reduction potential ( $E_{p,c}$ ) for 2-functionalized 1,3-dieethoxycarbonylazulenenes vs. the  $\sigma_p$  Hammett parameter of the substituent X.

being  $0.51 \pm 0.04$  V more positive compared to the average  $E_{p,c}$  of the monoazulenenes (Tables S5 and S6, ESI†). This is a consequence of the substantially greater resonance stabilization energy of the 6,6'-biazulenenic framework.

The molecular structure of **3a** is illustrated in Fig. 6. The two chemically identical, but crystallographically unique C–Cl bonds, C2–Cl1 and C2'–Cl2, within **3a** have the lengths of 1.674(2) Å and 1.682(2) Å, respectively. The longer C–Cl bond

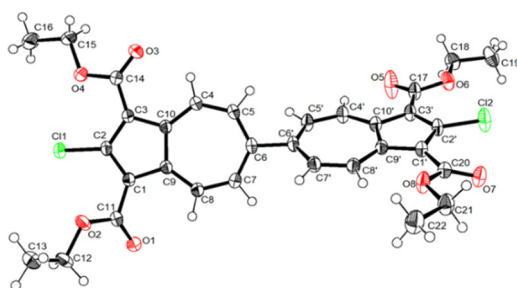


Fig. 6 Molecular structure of **3a** (50% thermal ellipsoids). Selected interatomic distances (Å) and dihedral angle (deg): C2–Cl1 1.674(2), C2'–Cl2 1.682(2), C6–C6' 1.478(2), C9–C10 1.437(2), C9'–C10' 1.440(3), O2...Cl1 2.918(2), O4...Cl1 2.834(1), O6...Cl2 2.816(2), O7...Cl2 2.876(2), C5–C6–C6'–C5' 48.1(2).

Table 1 Comparison of C(2)–Cl and C(9)–C(10) bond distances in X-ray structurally characterized 2-chloroazulenenic derivatives

Compound	$d(\text{C}^2\text{--Cl})$ Å	$d(\text{C}^9\text{--C}^{10})$ Å	CCDC identifier
	1.674(2)	1.437(2)	This work
	1.682(2)	1.440(3)	
	1.712(2)	1.471(2)	HOMRAE
	1.714(4)	1.470(6)	XIGPOU
	1.709(2)	1.470(3)	AYIDIX

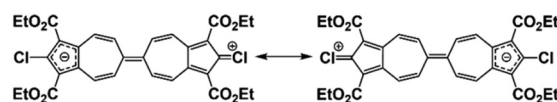


Fig. 7 Minor zwitterionic resonance forms of **3a**.

belongs to the half of the molecule featuring the shortest Cl...O contact (Cl2...O6) of 2.816 Å. Both C–Cl bonds in **3a** are significantly shorter than any C–Cl bond in all structurally characterized chloroazulenenes featuring Cl-substitution at the five-membered ring of the azulenic scaffold (Fig. S22 and Table S14, ESI†). In particular, the C–Cl bonds in **3a** are statistically shorter, per the 3- $\sigma$  criterion,<sup>32</sup> than those in the X-ray structures of the other three 2-chloroazulenenes known to date (Table 1).<sup>33–35</sup>

The C–Cl bond contractions in **3a** may be rationalized by invoking the minor heptafulvalene-like zwitterionic resonance forms depicted in Fig. 7, which show C=Cl double-bond character. This argument mirrors the crystallographic analysis of the chlorodiphenylmethyl cation by Laub *et al.*<sup>36</sup> The short C–Cl bond distance of 1.668(8) Å within this carbocation, which is statistically indistinguishable from those in **3a**, was attributed to chlorine back-donation exerting partial double-bond C=Cl<sup>+</sup> character (Fig. S23, ESI†).<sup>36</sup> Unusually short C–Cl bonds, including various C–Cl multiple bonding scenarios, continue to attract both experimental and theoretical interest.<sup>37–39</sup>

The C6–C6' bond distance of 1.478(2) Å within **3a** is markedly shorter than those in all other crystallographically characterized 6,6'-biazulenenes (Table 2).<sup>8,11,12,40</sup> In addition, as summarized in Table 2, the C–C bonds at the fusion of the five- and seven-membered rings in **3a** are substantially contracted as well. Both of these observations are consistent with a nontrivial heptafulvalene-like contribution to the structure of the biazenic scaffold of **3a**.<sup>41</sup> Moreover, the azulene–azulene interplanar angles in dichloro **3a** and diisocyano **4a**, which share the same 1,1',3'3'-tetraethoxycarbonyl-6,6'-biazenic core, are 48.1° and 66.9°,<sup>11</sup> respectively, although such comparison should be viewed *cum grano salis* as this torsion parameter is undoubtedly sensitive to crystal packing.

In summary, we demonstrated that the redox profile of the 6,6'-biazenic scaffold functionalized along its molecular axis is quantitatively tuneable within a wide window of potentials.



**Table 2** Comparison of C(6)–C(6') and C(9)–C(10) bond distances in X-ray structurally characterized 6,6'-biazulenenes

Compound	$d(\text{C}^6\text{--}\text{C}^{6'})$ , Å	$d(\text{C}^9\text{--}\text{C}^{10})$ , Å	CCDC identifier
	1.478(2)	1.437(2) 1.440(3)	This work
	1.498(2)	1.485(2) 1.488(2)	NAZROZ
	1.512(4)	1.475(3)	OSIGED
	1.497(3)	1.465(3)	HITRIP <sup>a</sup>
	1.499(3)	1.476(3)	

<sup>a</sup> Two crystallographically independent molecules in the asymmetric unit.

This was accomplished by considering, for the first time in the context of azulenic systems, the well documented  $\sigma_p$  Hammett parameters<sup>20</sup> reflecting the net electronic influence of the substituents. We anticipate that the facile access to the crystallographically unusual dichloro derivative **3a** offers not only new opportunities to engage the 6,6' architecture as an attractive molecular template in the realm of organic charge transfer and/or conductive materials, but also to explore unorthodox approaches for pursuing C–Cl multiple bonding.

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## Conflicts of interest

There are no conflicts to declare.

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