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## Thia-bridged triarylamine heterohelicene radical cations as redox-driven molecular switches<sup>†‡</sup>

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The first example of one-electron oxidation of thia-bridged triarylamine heterohelicenes to the corresponding exceptionally stable radical-cations, fully characterized, as hexafluoroantimonate salts, by means of UV-Vis, EPR, ENDOR, density functional theory calculations and X-ray analyses, is reported. Chemical and electro-chemical reversible redox processes are solidly demonstrated.

Triarylamines are probably the more utilized structural motifs among electron-donors for organic electronic devices (OED).<sup>1</sup> The possibility to design and prepare an almost unlimited combination of these compounds, using the Buckwald-Hartwig (B-H) nitrogen-carbon cross coupling, permitted the employment of proper substituted triarylamine in, *inter alia*, organic solar and photovoltaics cells,<sup>2</sup> organic light emission diode (OLED),<sup>3</sup> organic field-effect transistor (OFET)<sup>4</sup> and two photon devices.<sup>5</sup> Similarly, phenothiazines, beyond their value in medicinal chemistry,<sup>6</sup> have found applications in OED since the introduction of the sulfide bridge in diarylamine skeleton causes a further improvement of the molecule donor aptitude.<sup>7</sup> In this contest, particularly attractive appear thia-bridged triarylamines of type **1** (Fig. 1) both for their structure, a triarylamines skeleton forced in a helical shape by four *o,o'*-carbon-sulfur bonds, and for their electronic properties being, a *bis*-phenothiazine with an aromatic ring and a nitrogen atom in common. The preparation of parent compound **1** appeared in 2004 and foresees two intramolecular B-H processes.<sup>8</sup> Later we reported an original procedure for the synthesis of heterohelicenes of type **1** based on four consecutive regioselective electrophilic sulfur insertions<sup>9</sup> on a triarylamine scaffold, a methodology that has been recently applied for the preparation of compounds with potential application as organic dyes in dye-sensitized solar cells (DSSC).<sup>10</sup>

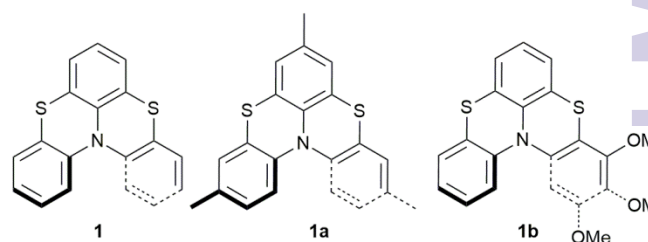


Fig. 1 General structure of thia-bridged heterohelicenes **1**.

In this communication we report a study carried out on two selected thia-bridged triarylamines, namely *C*<sub>2</sub> symmetric trimethyl derivative **1a** and asymmetric trimethoxy derivative **1b** (Fig. 1) concerning the synthesis and characterization of the corresponding remarkably stable radical-cations **1a**<sup>•+</sup> and **1b**<sup>•+</sup> isolated as hexafluoroantimonate salts.

The preparation of derivative **1a**, as already reported,<sup>9</sup> foresees the regioselective sulfenylation of tris-*p*-tolyl amine with two equivalents of phthalimidesulfonyl chloride (PhtNSCl, Pht = phthaloyl) followed by two intramolecular electrophilic aromatic substitutions (*i*S<sub>E</sub>Ar) promoted by AlCl<sub>3</sub>. Unsymmetrically substituted helicene **1b** was obtained in very good yield in two steps (suitable to be run one pot) using 10-(3,4,5-trimethoxyphenyl)-10H-phenothiazine as starting material that was regio- and chemoselectively sulfenylated with PhtNSCl and cyclized to **1b** with AlCl<sub>3</sub> (Experimental details for the preparation of helicene **1b** is available as ESI).

In the present study, we examined the redox-triggered molecular switching of **1a** and **1b** by both electrochemical and chemical oxidation into the corresponding radical cations **1a**<sup>•+</sup> and **1b**<sup>•+</sup>.

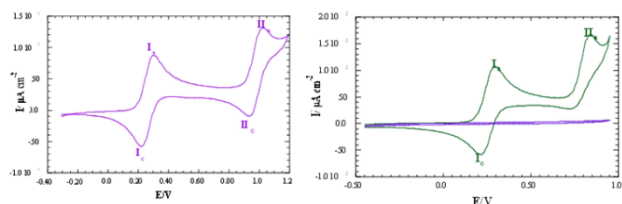
Initially, we studied the electron-transfer properties of **1a** and **1b** by electrochemical oxidation (See ESI for CV details). Cyclic voltammetry (CV) of **1a** and **1b** in a solvent electrolyte system, consisting of dichloromethane (DCM) and *t*-Bu<sub>4</sub>NPF<sub>6</sub>, shows for both helicenes a reversible wave at E<sub>1</sub><sup>o</sup> = +0.25 and +0.26 eV, respectively. These oxidation potentials are lower than those reported for the corresponding or similar substituted triarylamines.<sup>11</sup> Derivative **1a** showed a second reversible one-electron oxidation peak, at higher potential (E<sub>2</sub><sup>o</sup> = +1.05 eV), while helicene **1b** underwent an irreversible second oxidation process (Fig. 2).

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Experimental details, Experimental and calculated UV-Vis spectra, NMR spectra, EPR, ENDOR, theoretical calculations and crystallographic data for **1a**<sup>•+</sup> and **1b**<sup>•+</sup>.

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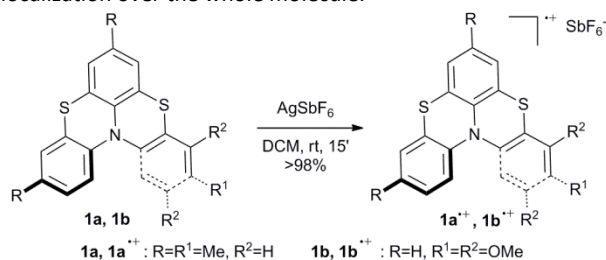
**Fig. 2** CVs as obtained in dichloromethane solution of 0.5 mM **1a** (left) and **1b** (right) in 0.2 M  $(t\text{-Bu})_4\text{NPF}_6$  at a potential scan rate of  $50\text{ mV s}^{-1}$ . Potentials are referred to the ferrocene/ferrocinium,  $\text{Fc}/\text{Fc}^+$  redox couple. In both cases two anodic peaks are observed. The low current line (in purple on the right) refers to the potential scan in the absence of electroactive species.

This is probably due to the well-known instability of *p*-unsubstituted triarylamines on the cyclic voltammetric time scale due to their rapid dimerization.<sup>12,13</sup> In analogy with the oxidation of triarylamines the first observed wave is expected to be the one-electron oxidation of **1a** and **1b** to radical cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** respectively. The easy reversible one-electron oxidation of triarylamines and phenothiazines is actually the basic feature for many of their electronic uses and indeed reasonable stable radical cations of such species have been obtained by electrochemical and chemical oxidation.<sup>13-15</sup>

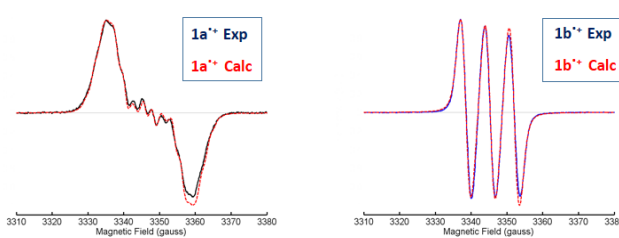
Thus we decided to investigate the one-electron chemical oxidation of thia-bridged heterohelicenes selecting  $\text{AgSbF}_6$  as the oxidant. When **1a** and **1b** were reacted in dry DCM with one equiv of  $\text{AgSbF}_6$  a deep coloured suspension (purple from **1a** and brilliant teal from **1b**) formed immediately. Filtering off the dark precipitate of  $\text{Ag}(0)$  and evaporating the DCM solution, allowed the isolation, in quantitative yields, of  $\text{SbF}_6^-$  radical-cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** as depicted in Scheme 1. Chemical and structural characterization of radical-cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** was achieved by elementary analysis, UV-Vis, EPR and ENDOR spectroscopy, density functional theory calculations and, eventually, X-ray.

Unlike helicenes, radical cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** show a broad absorption profile in the visible region. The theoretical calculations (CAM-B3LYP/cc-pVDZ) reproduced this situation. These absorptions can be related to the single electronic transitions to the SOMO from the closer fully occupied MOs (See ESI for details).

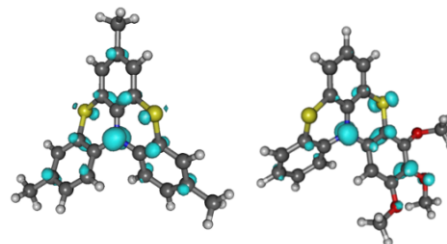
EPR spectra of radical cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** ( $10^{-4}\text{ M}$  in DCM) remained substantially unmodified in the range 180-310 K. In Fig. 3 are reported experimental and calculated EPR spectra of **1a<sup>•+</sup>** and **1b<sup>•+</sup>** recorded at 200 K, constants were obtained with Gaussian09. Calculations of *g* factors ( $g=2.0042$  and  $g=2.0056$  for **1a<sup>•+</sup>** and **1b<sup>•+</sup>** respectively) and hyperfine coupling and for **1b<sup>•+</sup>** further supported by ENDOR measurements are detailed in the ESI. EPR spectra showed that both radical-cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** exhibit spin delocalization over the whole molecule.



Scheme 1. Synthesis of radical-cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>** as  $\text{SbF}_6^-$  salts.



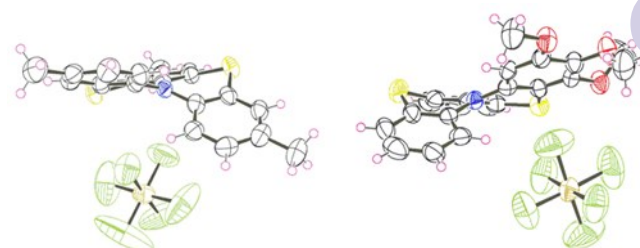
**Fig. 3** Experimental (black or blue) and calculated (red) EPR spectra of **1a<sup>•+</sup>** (left) and **1b<sup>•+</sup>** (right).



**Fig. 4** Calculated isodensity spin surfaces (cyan colors) (IsoValue of 0.07 AU) for **1a<sup>•+</sup>** (left) and **1b<sup>•+</sup>** (right).

The higher spin density is allocated on nitrogen, as indicated by *g* factors and hyperfine coupling constants. Indeed, as reported in Fig. 4, DFT calculations at the CAM-B3LYP/cc-DZVP level of theory show for both **1a<sup>•+</sup>** and **1b<sup>•+</sup>** radical-cations that the spin density is delocalized to all aryl moieties with a peak Mulliken spin density on the nitrogen atom of +0.36 and +0.29 electrons respectively (main Mulliken atomic spin densities for **1a<sup>•+</sup>** and **1b<sup>•+</sup>** are reported in Figure 4.SI-1 of the SI). Suitable crystals for X-Ray analysis of **1a<sup>•+</sup>** and **1b<sup>•+</sup>** were obtained by slow evaporation of DCM solutions enabling to undoubtedly confirm their structure (Fig. 5).

We have demonstrated<sup>9</sup> that the four long sulfur-carbon bonds bring a notable superimposition of terminal aryl rings in thia-bridged heterohelicenes **1** which represent a very rare example of configurationally stable [4]helicenes. Indeed, X-Ray of **1a** and **1b** showed dihedral angles between the planes containing the terminal aryl rings of  $61.4^\circ$  and  $70.8^\circ$  respectively.<sup>9</sup> Oxidation of helicenes to radical cations causes, in the crystal, a remarkable flattening<sup>16</sup> of the structures with a decrease of the helical bite. In fact, the aforementioned dihedral angles become  $52.2^\circ$  and  $54.5^\circ$  for **1a<sup>•+</sup>** and **1b<sup>•+</sup>** respectively, possibly as a consequence to better accommodate the delocalized spin density. In agreement with X-ray indications, optimized DFT/PMC geometries of the free molecules in DCM yield a decrease of  $8.5 \pm 2.5$  and  $9.2 \pm 3.5$  degrees for the aryl-aryl angles when passing from the neutral species **1a** and **1b** to the radical-cations **1a<sup>•+</sup>** and **1b<sup>•+</sup>**.



**Fig. 5** ORTEP drawing (thermal ellipsoids at 50% probability) of **1a<sup>•+</sup>** (left) and **1b<sup>•+</sup>** (right).

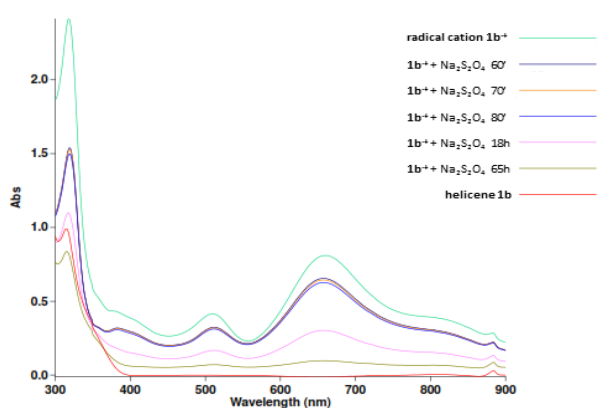


Fig. 6 UV/Vis absorptions during reduction of radical cation **1b**<sup>•+</sup> to neutral helicene **1b** with 40 equivs of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.

This suggest that the flattening of helical shape is not limited to the solid state. The possibility to obtain pretty stable radical-cations by oxidation of triarylamines or phenothiazines is well known.<sup>13-15</sup> At the same time, attempts to collect suitable crystals of triarylamine radical-cations for X-ray are rare, and radical-cations deriving from *p*-unsubstituted triaryl amine (i.e. like **1b**) are much less stable and prone to dimerization.<sup>13</sup> On the contrary, radical cations **1a**<sup>•+</sup> and **1b**<sup>•+</sup> demonstrated to be exceptionally stable either in the solid state (more than two years under air at rt) and in solution. As it occurs during CV, we also demonstrated the reversibility of chemical red-ox processes, reducing radical cations **1a**<sup>•+</sup> and **1b**<sup>•+</sup> to the corresponding helicenes **1a** and **1b** with an excess (40 equivs) of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at rt for, roughly, 65h. In Fig. 6 is reported the reduction process of **1b**<sup>•+</sup> followed by UV-Vis spectroscopy. Remarkably, further demonstrating the stability of these radical cations and in particular of **1b**<sup>•+</sup> bearing two unsubstituted positions *para* to the nitrogen, helicenes **1a** and **1b**, obtained by reduction of the radical-cations with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, were again oxidized with AgSbF<sub>6</sub> without any appreciable difference between UV-Vis spectra of **1a**<sup>•+</sup> and **1b**<sup>•+</sup> obtained after the first or the second red-ox cycle.

In conclusion, this work provides the first example of one-electron oxidation of stable thia-bridged triarylamine heterohelicenes to the corresponding radical-cations which were fully characterized and showed a remarkable stability either as crystals or in solution. The possibility to obtain these peculiar species as single enantiomers open the way to the construction of OED devices including redox-triggered chiroptical switches that is currently under investigation.

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