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# From Hexaoxy-[6]Pericyclynes to *Carbo*-Cyclohexadienes, *Carbo*-Benzenes, and Dihydro-*Carbo*-Benzenes: Synthesis, Structure, and Chromophoric and Redox Properties

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Abstract: When targeting the quadrupolar p-dianisyltetraphenyl-carbo-benzene by reductive treatment of a hexaoxy-[6]pericyclyne precursor 3 with SnCl<sub>2</sub>/HCl, a strict control of the conditions allowed for the isolation of three C<sub>18</sub>-macrocyclic products: the targeted aromatic carbo-benzene 1, a sub-reduced non-aromatic carbo-cyclohexadiene 4A, and an over-reduced aromatic dihydro-carbo-benzene 5A. Each of them was fully characterized by its absorption and NMR spectra, which were interpreted by comparison with calculated spectra from static structures optimized at the DFT level. According to the nucleus-independent chemical shift (NICS) value (NICS  $\approx$  -13 ppm), the macrocyclic aromaticity of 5A is indicated to be equivalent to that of 1. This is confirmed by the strong NMR spectroscopic deshielding of the *ortho*-*CH* protons of the aryl substituents, but also by the strong shielding of the internal proton of the endocyclic *trans*-CH=CH double bond that results from the hydrogenation of one of the C=C bonds of **3**. Both the aromatics **1** and **5A** exhibit a high crystallinity, revealed by SEM and TEM images, which allowed for a structural determination by using an X-ray microsource. A good agreement with calculated molecular structures was found, and columnar assemblies of the C<sub>18</sub> macrocycles were

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evidenced in the crystal packing. The non-aromatic carbo-cyclohexadiene 4A is shown to be an intermediate in the formation of 1 from 3. It exhibits a remarkable dichromism in solution, which is related to the occurrence of two intense bands in the visible region of its UV/Vis spectrum. These properties could be attributed to the dibutatrienylacetylene (DBA) unit that occurs in the three chromophores, but which is not involved in a macrocyclic  $\pi$ -delocalization in **4A** only. A versatile redox behavior of the carbo-chromophores is evidenced by cyclic voltammetry and was analyzed by calculation of the ionization potential, electron affinity, and frontier molecular orbitals.

#### Introduction

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102993. It includes experimental procedures and characterization data for 1, 3, 4A, and 5A. Calculated structures and absorption spectra and NMR spectroscopic data for 1, 4A, 4B, and 5A. X-ray diffraction analysis data for 5A.

The definition of  $carbo_k$ -merization, that is, the systematic insertion of  $C_{2k}$  units and corresponding 4k reactive  $\pi$  electrons into all the bonds of a Lewis structure,<sup>[1]</sup> raises the basic question of their chemical stability, even for the first generation (k=1) that is henceforth addressed.<sup>[2]</sup> Three types of C<sub>2</sub> units that differ in intrinsic stability can be distinguished: the acetylene type (A-C=C-B), the butatriene type (A=C=C=B), and the diacetylene type (A=C-C=B). In the cyclic series,<sup>[3]</sup> the so-called "ring carbo-mers" of the first kind (with acetylenic C2 units only) were exemplified early on by Scott's [n]pericyclynes, the ring carbo-mers of [n]cycloalkanes,<sup>[4]</sup> which were later on generalized to oxyfunctional versions:<sup>[5,6]</sup> in spite of the vicinity of the  $nC_2$ units, the relative stability of small [n] pericyclynes  $(n \ge 4)$ can be explained by a relaxative bending at the -sp-C- centers, and by steric insulation of the triple bonds between the propargylic substituents.<sup>[1b,7]</sup> Compared to alkynes, butatrienic molecules are less available (butatriene itself is less stable than its butenyne isomer),<sup>[8]</sup> and carbo-mers of the

second kind (which contain butatrienic C<sub>2</sub> units) are mainly found in the family of the ring carbo-mers of benzene (routinely called "carbo-benzenes"),<sup>[9]</sup> in which the butatriene edges are stabilized by resonance of the two equivalent Kekulè structures of the C<sub>18</sub> carbo-benzene ring.<sup>[1b,5,9]</sup> This macrocycle indeed satisfies the Hückel rule just as the parent C<sub>6</sub> benzene ring does and proved to be definitely aromatic according to various calculated structural, magnetic, and energetic indices.<sup>[10]</sup> In the dozen substituted carbo-benzene representatives synthesized to date, the aromaticity is revealed by their stability, by the planarity and symmetry of the C<sub>18</sub> ring, and by a strong NMR signal of peripheral <sup>1</sup>H nuclei.[6d,11] All these carbo-benzenes have been obtained by reductive aromatization of hexaoxy-[6]pericyclynes.[5,6d,11] An optimal route to the subfamily of centrosymmetric 1,10disubstituted carbo-benzenes, such as p-dianisyltetraphenylcarbo-benzene (1), involves the [6]pericyclynedione key-intermediate 2, the synthesis of which has been recently optimized (Scheme 1).<sup>[12]</sup> The target **1** was selected for its strong



Scheme 1. Targeted quadrupolar *carbo*-benzenic chromophore from a [6]pericyclynedione.<sup>[12,13]</sup>

quadrupolar character (with a calculated maximal diagonal element  $Q_{zz}$  of the quadrupole tensor of -340 versus -317 D.Å for hexaphenyl-*carbo*-benzene) and anticipated chromophoric properties (in particular in nonlinear optics), and an unusual outcome of the classical methodology envisaged for its synthesis was mentioned.<sup>[13]</sup> Among the side products, indeed a ring *carbo*-mer of cyclohexadiene stands as the first example of non-aromatic ring *carbo*-mer of the second kind. Full results are reported hereafter, in which the characterization and physicochemical properties of three types of unprecedented chromophores are compared and discussed on the basis of joint experimental and computational studies.

#### **Results and Discussion**

Synthesis of 1 and derivatives thereof: The known [6]pericyclynedione 2 was prepared in nine steps and 7% overall yield from *trans*-1,2-dibenzoylethene and was obtained as a quasi-statistical mixture of its five diastereoisomers, which could be partly resolved by semi-preparative HPLC techniques.<sup>[12]</sup> The unresolved mixture underwent double nucleophilic attack by *p*-anisylmagnesium bromide (2 equiv) to give the expected pericyclynediol **3** as a mixture of diastereoisomers (14 in theory) in 76% yield (Scheme 2).



Scheme 2. Preparation of [6]pericyclynediol 3 (mixture of stereoisomers).

This mixture was then submitted to the reducing system SnCl<sub>2</sub>/HCl.<sup>[8]</sup> To minimize undesired transformations of the  $\pi$ -electron-rich system of **3** (in particular, polymerization), the reduction was carried out at low temperature in diethyl ether, in which the acidity of HCl is moderate. The solution turned to green at -60 °C, and then reversibly to dark red at -50°C. TLC monitoring (petroleum ether/CHCl<sub>3</sub> 2:8) displayed several highly colored spots: green ( $R_f \approx 0.25$  and 0.30), purple ( $R_{\rm f} \approx 0.62$ ), and orange-red ( $R_{\rm f} \approx 0.69$ ). After 3 h at -50 °C, the medium was treated with 1 M aqueous sodium hydroxide, then extracted with diethyl ether, and the organic layer was evaporated to dryness. The dark green oily residue was purified by two successive column chromatography runs over silica gel (eluted with chloroform and chloroform/heptane 7:3), followed by a separation using semi-preparative HPLC techniques. Three fractions of pure products 1, 4, and 5 were isolated, the two latter initially presenting structural ambiguity (Scheme 3). The determination of their exact structures (more or less reduced with respect to the initial target 1) and properties are detailed below.

**Characterization of 1**: The product of the less polar fraction  $(R_f \approx 0.69)$  was obtained as an air-stable green-gold solid that turned red in solution. MALDI-TOF MS analysis indicated a single molecular peak at m/z 738.26 uma that corresponded to the targeted *carbo*-benzene **1**, which was thus isolated in 8% yield. In a solution of **1** in CDCl<sub>3</sub>, two <sup>1</sup>H NMR doublets at  $\delta = 9.47$  and 9.42 ppm in a 2:1 integration ratio were assigned to the *ortho*-CH protons of the respective phenyl and anisyl substituents that experienced the characteristic deshielding by the strong diatropic ring current of the C<sub>18</sub> ring. In spite of a weak solubility, a consistent <sup>13</sup>C NMR spectrum could be recorded by using [Cr(acac)<sub>3</sub>] (acac=acetylacetonate) as a relaxation agent, thereby allowing for the detection of the requested number of quaternary carbon signals.

As X-ray diffraction analysis of crystals of **1** appeared first impracticable (see below), the structure of **1** was investigated at the B3PW91/6-31G<sup>\*\*</sup> level of calculation. Several conformations close in energy were obtained on the singlet spin-state potential energy surface (the lowest triplet spin state of **1** was found to be 26.16 kcal mol<sup>-1</sup> higher in energy,



Scheme 3. Outcome of a reductive treatment (SnCl<sub>2</sub>/HCl) of pericyclynediol 3.

with a zero-point energy (ZPE)-corrected value of 24.00 kcal mol<sup>-1</sup>). The totally planar structure of  $C_{2h}$  symmetry is a seventh-order saddle point that lies 6.34 kcal mol<sup>-1</sup> higher in energy than the  $C_2$ -symmetric minimum that exhibits aryl substituents tilted by around  $(18.5 \pm 1.3)^\circ$  with respect to the quasi-planar  $C_{18}$  macrocycle in a helical way (see Figure S4 in the Supporting Information).

The  $C_2$ -symmetric conformation is degenerated in energy  $(\Delta E = +0.03 \text{ kcal mol}^{-1})$  with another dipolar conformation with "syn" methoxy groups, hereafter referred to as  $C_1$ -syn. The  $C_2$ -symmetric global minimum was calculated to be quasi-isoenergetic with a  $C_i$ -symmetric conformer ( $\Delta E = +$  0.88 kcal mol<sup>-1</sup>) that exhibits anisyl substituents almost coplanar with the  $C_{18}$  macrocycle and parallel phenyl substituents tilted by 21°. This latter quadrupolar conformation is almost identical to the experimental conformation finally found in the crystal state (see below).

The calculated structure of **1** (Figure S4 in the Supporting Information) allowed for further calculations of spectroscopic properties and confrontation with experimental data. With regards to NMR spectroscopy, an assignment of all the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic signals of **1** could be thus proposed on the basis of <sup>1</sup>H-<sup>1</sup>H COSY-45, <sup>13</sup>C-<sup>1</sup>H heteronuclear single-quantum correlation (HSQC), and heteronuclear multiple-bond correlation (HMBC) experiments (Figure 1). This assignment was confirmed by comparison with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic chemical shifts calculated at the B3PW91/6-31+G\*\* level by using the gauge-independent atomic orbital (GIAO) methodology.<sup>[14]</sup> As previously observed for other *carbo*-benzene derivatives,<sup>[11]</sup> the agreement is remarkable, in particular for all the <sup>13</sup>C chemical shifts (Figure 1).<sup>[15]</sup>



Figure 1. Experimental and calculated  ${}^{1}H$  and  ${}^{13}C$  chemical shifts [ppm] of 1 (B3PW91/6-31+G\*\* level).<sup>[15]</sup>

As observed in other phenyl-substituted carbo-benzenes,<sup>[11]</sup> whereas the o-<sup>1</sup>H nuclei of the phenyl substituents of 1 undergo a strong deshielding by the macrocyclic ring current ( $\delta = 9.47$  versus 7.59 ppm in biphenyl), the *ipso*-<sup>13</sup>C nuclei do not ( $\delta = 140.4$  ppm in **1** versus  $\delta = 140.8$  ppm in biphenyl). Further insight into the magnetic aromaticity of the  $C_{18}$  ring and the role played by the phenyl substituents was appraised from the nucleus-independent chemical shift (NICS) at the geometric center of the macrocycle. The calculated value for 1 ( $C_{18}An_2Ph_4$ ), NICS = -13.5 ppm, is identical to the corresponding value for hexaphenyl-carbo-benzene (C<sub>18</sub>Ph<sub>6</sub>), but is significantly lower than the values found for unsubstituted *carbo*-benzene ( $C_{18}H_6$ : NICS = -17.9 ppm) or unsubstituted *p*-dianisyl-carbo-benzene  $(C_{18}An_{2}H_{4}: NICS = -15.9 \text{ ppm})$  at the same B3PW91/6-31 + G\*\* level of calculation.<sup>[11,13]</sup> The present results confirm that the magnetic aromaticity of the carbo-benzene ring is

highly sensitive to aryl substitution, and indicate that anisyl and phenyl substituents have similar effects. In a symmetric manner, and rather unexpectedly, the NICS values calculated at the geometric center of the phenyl (NICS = -5.4 ppm) or anisyl (NICS = -6.1 ppm) substituents of **1** are also significantly lowered relative to benzene (NICS = -8.0 ppm).

The absorption spectrum of **1** in CHCl<sub>3</sub> displays an intense band at  $\lambda_{max} = 482 \text{ nm}$  ( $\varepsilon = 222112 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ), a weaker band at  $\lambda' = 525 \text{ nm}$  (with a shoulder at 540 nm), and a very weak band at  $\lambda'' = 580 \text{ nm}$  (Figure S1 in the Supporting Information). By analogy with the Soret and Q bands of porphyrins, these main patterns and ranges of wavelengths constitute a signature of the *carbo*-benzene macrocycle,<sup>[16]</sup> and the present results confirm previous observations that the  $\lambda_{max}$  value is poorly sensitive to the substituents (phenyl, 4-anisyl, 4-pyridyl) of hexaaryl-*carbo*-benzenes (472 nm for C<sub>18</sub>Ph<sub>6</sub>).<sup>[5,11]</sup> The spectrum of **1** was calculated in the gas phase for the  $C_2$ -symmetric geometry of minimum energy. Both ZINDO and TDB3PW91 calculations are in good agreement with the experimental data (Figure 2), in particu-



Figure 2. Absorption spectra (absorbance versus energy) of **1** calculated at the semi-empirical ZINDO and TDB3PW91/6-31G\*\* levels. Simulation with Gaussian-shaped bands of 0.09919 eV half bandwidth. The reference experimental spectrum of **1** (experimental (EXPTL), in CHCl<sub>3</sub>) is also given (see Figure S1a in the Supporting Information).

lar with regards to the absolute  $\lambda_{max}$  value for the time-dependent DFT (TDDFT) calculation (482 nm). It is also noteworthy that TDDFT calculations performed on alternative conformations of **1** (with  $C_1$ -syn,  $C_i$ , or  $C_2$  symmetry), which are likely to be also present in the experimental solution, afford virtually the same spectrum.

The calculated transition energy of largest oscillator strength (2.5683 eV) is in good agreement with that of the strongest experimental band (2.5722 eV) and is compatible with the mean error range of TDDFT calculations (0.3–0.4 eV).<sup>[17]</sup> This absorption band is actually related to two quasi-degenerate vertical transitions (see Figure S5 in the

Supporting Information) from the ground state  $|S_0\rangle$  to singlet excited states  $|S_3\rangle$  and  $|S_4\rangle$ , respectively (Table S2 in the Supporting Information). As in the Gouterman four-orbital model invoked for the explanation of the electronic spectra of porphyrins,<sup>[18]</sup> these transitions involve mainly two one-electron excitations from one of the two HOMOs to one of the two LUMOs of **1** in the  $C_2$ -symmetric geometry. As these orbitals are mostly localized over the  $C_{18}$  ring, these excitations do not exhibit any charge-transfer character and the corresponding transition densities are confined inside the macrocycle (Figure S6 in the Supporting Information).

The weak experimental absorption bands at 525 nm (2.3615 eV) and 580 nm (2.1376 eV) do not show up in the calculated spectra of **1** at either the TDDFT or the ZINDO level (Figure 2). The transitions from the ground state to the first singlet excited states  $|S_1>$  and  $|S_2>$ , calculated at 731.5 and 630.1 nm, respectively, at the TDB3PW91/631G\*\* level, are indeed out of range and exhibit very small oscillator strengths (Table S2 in the Supporting Information). These weak absorption bands cannot be ascribed to the dynamic behavior of **1** because the calculated absorption spectra are insensitive to the conformation of **1**.

The first singlet excited states,  $|S_1\rangle$  and  $|S_4\rangle$  on one hand, and  $|S_2\rangle$  and  $|S_3\rangle$  on the other, are described by combinations of the same one-electron excitations, adding or canceling each other (Table S2 in the Supporting Information). This picture actually fits with the Gouterman fourorbital model for porphyrins, which predicts strongly allowed transitions to the higher excited states (Soret band) and weakly allowed transitions to the lower excited states (Q bands). One possible interpretation for the failure of the calculation to reproduce the weak experimental bands would be that they correspond to the Q bands of porphyrins, that is, to transitions from the ground state  $|S_0\rangle$  to the lowlying excited states  $|S_1\rangle$  and  $|S_2\rangle$ , but that TDDFT fails to predict their range. Multireference configuration interaction calculations are underway to refine this interpretation.

As mentioned above, crystals of 1 were repeatedly obtained from various solvent mixtures, but their minute size and low diffracting power long prevented any structural determination by X-ray crystallography. The high crystallinity of 1 was, however, illustrated by SEM images of golden flakelike crystals obtained by slow diffusion of methanol into a chloroform solution of 1 (Figure 3). The regular form of the microcrystals (mostly smooth and thin rectangles or squares) suggested their single-crystal nature and encouraged further efforts in X-ray crystallography.

After many unsuccessful attempts, the X-ray crystal structure of **1** could finally be determined with a satisfactory reliability factor ( $R_1$  ( $I > 2\sigma(I)$ )=0.0481) by using an X-ray microsource ( $\lambda$ =0.71073 Å) on single crystals deposited from a 1:1 CHCl<sub>3</sub>/C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> solution (Figure 4). Within the estimated standard deviation (ESD) errors for interatomic distances and angles, the structural data in the crystal state are almost identical with the DFT-calculated ones in the gas phase (Figure S4 in the Supporting Information). The mac-



Figure 3. SEM images of crystals of 1.



Figure 4. Molecular view of the X-ray crystal structure of 1, with thermal ellipsoids drawn at the 50% probability level (for clarity, the hydrogen atoms are omitted). Space group:  $P2_1/c$ ,  $R_1$  ( $I > 2\sigma(I)$ ) = 0.0481 (Table S1 in the Supporting Information). Selected bond lengths [Å]: C1-C2= 1.389(4), C2-C3=1.387(4), C2-C10=1.470(4), C3-C4=1.223(4), C4-C5 = 1.384(4), C5 - C6 = 1.380(4), C5 - C17 = 1.477(4), C6 - C7 = 1.226(4),C7-C8=1.383(4), C8-9=1.388(4), C8-C23=1.479(4). Selected bond angles [°]: C13-O1-C16=117.5(2), C9A-C1-C2=177.2(3), C3-C2-C1= C3-C2-C10=120.6(2), C1-C2-C10=121.9(2), C4-C3-C2= 117.5(2). 176.8(3), C3-C4-C5 = 176.9(3),C6-C5-C4=119.7(2), C6-C5-C17 = C4-C5-C17 = 120.8(2),C7-C6-C5 = 174.9(3),C6-C7-C8= 119.5(2), 177.4(3), C7-C8-C9=119.7(2).

rocycle is indeed found to be quasi-planar, and the C–C bond lengths differ by at most  $\pm\,0.01\,\text{\AA}$  from those that

occur in the calculated structure of  $C_2$  symmetry (Figure S4 in the Supporting Information). Likewise, the experimental torsion angles between the C<sub>18</sub> macrocycle and aryl substituents (-18.4, 0.3, 17.1°) differ from those of the calculated  $C_2$ -symmetric structure by at most  $\pm 17^\circ$  for the anisyl substituents, and by at most  $\pm 3^\circ$  for the phenyl substituents.

In the crystal, the macrocycles of **1** stack in regular hexagonal columns (the axis of a column being aligned with the normal of the macrocycles), in which two successive  $C_{18}$  sections are separated by 7.34 Å. In a given column, phenyl substituents of two neighboring columns intercalate by weak  $\pi$ -stacking as indicated by short contacts between *ortho*carbon atoms and  $C_2$  units of two successive  $C_{18}$  rings. The crystal packing involves disordered 1,2-dichloroethane molecules outside the columns and thus differs from previously reported hexagonal packing of other *carbo*-benzenic or [6]pericyclynic derivatives, in which chlorinated solvent molecules (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) intercalate inside columns of  $C_{18}$ macrocycles.<sup>[5b, 6d, 11, 19]</sup>

of 1,10-dianisyldimethoxytetraphenyl-Characterization carbo-cyclohexadiene (4): The <sup>1</sup>H NMR spectrum of the more polar fraction that corresponds to the most polar green TLC spot ( $R_{\rm f} \approx 0.25$  and 0.30) displayed two pairs of  $OCH_3$  signals in a 55:45 ratio in the region of the methoxy substituents of the [6]pericyclynic precursor 3, namely, at  $\delta = 3.65$  and 3.77 ppm, respectively. A partial reduction of **3** was therefore anticipated, and indeed the molecular peak at m/z 800.39 uma of the MALDI-TOF spectrum was compatible with the doubly reduced species 4A or 4B, which occur as pairs of diastereoisomers (Scheme 4). The doubly reduced products 4C and 4D (in which at least one of the anisyl substituents is not conjugated with a butatriene edge of the macrocycle) could thus be ruled out, but the <sup>1</sup>H and <sup>13</sup>C NMR spectra did not allow us to discriminate between the regioisomers **4A** and **4B**.

As many attempts failed to produce single crystals from the mixture of stereoisomers of 4, the structures of both the possible diastereoisomers of 4A and 4B were calculated at the B3PW91/6-31G\*\* level. The four isomers were found to accommodate quasi-isoenergetic twist, boat or chair conformations of the C<sub>18</sub> macrocycle, with the most stable conformers ranking in the order *trans*-4A (0.0) < *cis*-4B (0.4) < *trans*-4B (1.1) < *cis*-4A (1.5), in which the relative energy values given in brackets are in kcal mol<sup>-1</sup>. Whereas the boat conformation of *cis*-4B and *trans*-4B allows for the *trans*-annular coplanarity of the non-conjugated C<sub>4</sub> butatriene edges, the twisted conformation of *cis*-4A and *trans*-4A results in a dihedral angle between the conjugated butatriene edges of 18.0 and 19.2°, respectively (Figure 5).

The absorption spectrum in chloroform of the product **4** (Scheme 3) displays two strong absorption bands at 437.4 nm and  $\lambda_{max} = 602.3$  nm ( $\varepsilon = 41943 \text{ mol L}^{-1} \text{ cm}^{-1}$ ; Figure S1 in the Supporting Information). The absorption spectra of the *cis*- or *trans*-diastereoisomers of the regioisomers **4A** and **4B** were also calculated at the ZINDO and TDDFT levels in the gas phase (Figure 6a and b).

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Scheme 4. A priori possible bis-butatrienic structures for product 4 resulting from partial reduction of the pericyclynic precursor 3 (Scheme 3). Each of them corresponds to *cis* and *trans* diastereoisomers. Only the regioisomers 4A and 4B, in which both the anisyl substituents are conjugated with a butatriene edge, were shown to be compatible with MALDI-TOF analysis (m/z 800.39 uma).

At the TDB3PW91 level, the spectra of the **4A**-type regioisomers exhibit two strong bands of comparable oscillator strength, the transition energies of which are close to the experimental ones (f=0.9209, 2.8505 eV=435.0 nm versus 2.8345 eV=437.4 nm; f=0.7497, 1.8481 eV=670.9 nm versus 2.0584 eV=602.3 nm). The spectra of the *cis*- and *trans*-diastereoisomers are almost superimposable. These transitions involve excitations from the ground state  $|S_0>$  to the first excited state  $|S_1>(0.71 \text{ H}\rightarrow\text{L})$  and third excited state  $|S_3>(0.54 \text{ H}\rightarrow\text{L}+1+0.43 \text{ H}-1\rightarrow\text{L})$ . Similar results were obtained at the ZINDO level, with an even better fit for the bathochromic absorption (see Table S3 in Supporting Information).

On the other hand, the TDDFT spectra of the **4B**-type regioisomers exhibit only one strong absorption band at 449 nm (similar values are calculated at the TDB3PW91/6-31G\*\* level: f=1.7396, 2.7448 eV=451.7 nm, and at the ZINDO level: f=2.5204, 2.7779 eV=446.3 nm). It corresponds to an excitation from the ground state to the  $|S_4>$ 



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Figure 5. Side view of the calculated structures of the *cis* and *trans* diastereoisomers of regioisomers **4A** and **4B** (see Scheme 4). Front views are given in Figure S7 in the Supporting Information. B3PW91/6-31G\*\* level

singlet excited state  $(0.56 \text{ H} \rightarrow \text{L}+1-0.43 \text{ H}-1 \rightarrow \text{L};$  see Table S4 in the Supporting Information).

of calculation. Relative energies are given in kcal mol<sup>-1</sup>.

The striking difference between the calculated UV/Vis spectra of the regioisomers **4A** and **4B**, and the remarkable fit of the experimental pattern with the two-band pattern of **4A**, allows us to assign the regiochemistry of the product **4** to that of **4A**, which corresponds to the largest conjugation extent (in which the two butatriene edges are conjugated



Figure 6. Calculated absorption spectra (absorbance versus energy) of the *carbo*-cyclohexadienes 4, 4A, and 4B. a) TDB3PW91/6-31G\*\* level for the four isomers *trans*-4A, *cis*-4A, *trans*-4B, and *cis*-4B in the gas phase. b) ZINDO level for the *cis* diastereoisomers of the regioisomers of 4A and 4B in the gas phase. Simulation with Gaussian-shaped bands of 0.09919 eV half bandwidth. The reference experimental spectrum of 4=4A (experiment, in CHCl<sub>3</sub>) is also given (see Figure S1b in the Supporting Information).

through a butyne edge and conjugated with both the anisyl substituents). This illustrates how theoretical calculations can be useful for the determination of molecular structures in the absence of X-ray diffraction data.

The <sup>1</sup>H and <sup>13</sup>C NMR and <sup>1</sup>H-<sup>13</sup>C HMBC spectra of the mixture of stereoisomers of **4** are fully consistent with the regioisomer **4A**, but also with the regioisomer **4B** (see the Experimental Section in the Supporting Information). To confirm the above assignment 4=4A, the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic chemical shifts of the *cis*- and *trans*-diastereo-isomers of both **4A** and **4B** were calculated at the B3PW91/6-31+G\*\* level, and those of the nuclei that became equivalent on the experimental NMR spectroscopic timescale at

room temperature were averaged, as was done for the *carbo*-benzene **1** (see above, Figure 1).<sup>[15]</sup> Both sets of results are, however, compatible with the experimental data within the error range (see Figure 7 and Figure S8 in the Support-



Figure 7. Experimental and calculated <sup>1</sup>H and <sup>13</sup>C chemical shifts [ppm] of the *carbo*-cyclohexadienes *trans*-**4A** and *cis*-**4A** (B3PW91/6-31+G\*\*). The averaging treatment is the one used for *carbo*-benzene **1** (Figure 1).<sup>[15]</sup>

ing Information). The only noticeable difference concerns the <sup>13</sup>C chemical shifts of the sp-carbon atoms of the butatriene moieties, which are predicted to occur at slightly lower field in **4B** ( $\delta$ =148.5, 149.8, 147.2, and 150.8 ppm for *trans*-**4B**; see Figure S8 in the Supporting Information) than in **4A** ( $\delta$ =141.1 and 147.7 ppm for *trans*-**4A**;  $\delta$ =142.7 and 147.5 ppm for *cis*-**4A**; see Figure 7). The experimental data ( $\delta$ =144.7, 144.8, 147.1, and 147.2 ppm) are closer to the calculated values for **4A** than to the calculated values for **4B**. Although assignment of the experimental regioisomer to the structure **4A** (instead of **4B**) would be presumptuous on the sole basis of such small differences in chemical shifts ( $\delta \approx 3$ -6 ppm), the NMR spectroscopic results tend to confirm the assignment **4**=**4A** on the basis of the comparison of the calculated absorption spectra of **4A** and **4B**.

Finally, semi-preparative HPLC separation of mixture **4** afforded pure fractions of the diastereoisomers *trans*-**4A** and *cis*-**4A**, the NMR spectra of which could thus be record-

ed separately (Figure S2 in the Supporting Information). Although the stereoisomers *trans*-**4A** and *cis*-**4A** could not be unambiguously assigned, their respective signature is given by the two types of PhC–OCH<sub>3</sub> and phenyl *o*-CH <sup>1</sup>H chemical shifts. The two sets of experimental values { $\delta$ =3.65, 7.90 ppm} and { $\delta$ =3.77,

7.83 ppm} are tentatively assigned on the basis of the corresponding calculated <sup>1</sup>H chemical shifts to *trans*-**4A** ( $\delta$ =3.39, 8.40 ppm) and *cis*-**4A** ( $\delta$ =3.70, 8.25 ppm), respectively (Figure 7). On the basis of these results, the product of the less (respectively more) polar fraction of **4** is therefore tentatively assigned to *trans*-**4A** (respectively *cis*-**4A**).

It is finally noteworthy that the *o*-CH nuclei of the phenyl and anisyl substituents of the dibutatrienylacetylene (DBA) unit resonate at higher field in **4A** ( $\delta$ =7.90 and 7.76 ppm, respectively) than in **1** ( $\delta$ =9.47 and 9.42 ppm, respectively). This is the anticipated consequence of the non-aromatic character of the macrocycle of **4A**, which is confirmed by the calculation of a quasi-vanishing NICS value of  $\delta$ = + 1.15 ppm for *trans*-**4A** (versus  $\delta$ =-13.5 ppm for **1**).

The *carbo*-cyclohexadienes **4A** that result from a fourelectron reduction of the pericyclynediol **3** are likely intermediates in the six-electron reductive aromatization that leads to the *carbo*-benzene **1**. The reactivity of **4A** in the prolonged presence of the SnCl<sub>2</sub>/HCl reducing system was monitored by <sup>1</sup>H NMR spectroscopy. A solution of **4A** in CDCl<sub>3</sub> was thus treated with SnCl<sub>2</sub> and DCl in D<sub>2</sub>O directly in an NMR spectroscopy tube for one night at room temperature. The initial dark green of the organic layer turned slowly to deep red, and the <sup>1</sup>H NMR spectrum of the crude mixture confirmed the total conversion of the *carbo*-cyclohexadiene **4A** to *carbo*-benzene **1** (Scheme 5).

The highly conjugated but non-aromatic pseudo-quadrupolar character of the *carbo*-cyclohexadiene 4A is to be related to the unusual occurrence of two strong absorption bands of similar intensities in complementary blue and red



Scheme 5. Quantitative reductive aromatization of *carbo*-cyclohexadiene **4A** (mixture of stereoisomers) into *carbo*-benzene **1**, as monitored in situ by <sup>1</sup>H NMR spectroscopy.

regions of the visible spectrum (Figure 6). This unusual spectroscopic property is also to be related with an unusual chromophoric property of 4A, namely, a remarkable dichromism when dissolved in most classical organic solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, toluene, and so on).<sup>[20]</sup> Such diluted solutions indeed appear turquoise-blue through short optical paths, and deep purple through longer optical paths (Figure 8). In spite of its fascinating visual effect, and likely because of its rareness,<sup>[21]</sup> the solution dichromism of pure organic molecules has been sporadically addressed in the literature.<sup>[20]</sup> Although the visual effect might also have been a priori explained by a fluorescence phenomenon (possibly overcoming the absorption of incident light at long optical path in the orthogonal direction), the emission spectrum of 4A evidenced such a weak fluorescence (in the green region with a Stokes shift of 116 nm) that it cannot be invoked for the phenomenon (Figure 8).<sup>[22]</sup> The dichromic property of 4A is actually explained by the intensity and sharpness of the absorption bands at 437 and 602 nm: it is correlated with the relative position of the absorption wavelengths of **4A** and the region of high sensitivity of the human eye in the chromatic diagram (Figure 8).<sup>[21b]</sup>

**Characterization of** *p***-dianisyltetraphenyldihydro**-*carbo*-benzene (5): The third fraction isolated by HPLC (Scheme 3) and that corresponds to the violet TLC spot of intermediate polarity ( $R_f$ =0.62) afforded a dark violet stable crystalline solid 5 (Scheme 3) soluble in most organic solvents. The MALDI-TOF mass spectrum of 5 indicated a molecular mass of 740.2 versus 738.2 uma for the *carbo*-benzene 1,



Figure 8. Illustration of the dichromism of a solution of dianisyl-*carbo*-cyclohexadiene **4A** in chloroform appearing turquoise-blue at short optical path (left) and deep purple at long optical path (right). The corresponding schematic interpretations, namely, "soustractive" (perception of a complementary color at short optical path) or "additive" (perception of the superimposition of pure chromatic colors at long optical path), depends on the regions of the human eye sensitivity (middle).<sup>[20b]</sup>

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thereby suggesting that 5 is a dihydrogenated derivative of 1, namely, a dihydro-carbo-benzene, which was thus isolated in 6% yield. The <sup>1</sup>H NMR spectrum of 5 showed highly deshielded signals in the range  $\delta = 8.50 - 9.20$  ppm for *ortho* protons of phenyl and anisyl substituents, thus evidencing that the C<sub>18</sub> macrocycle is as aromatic as in the carbo-benzene 1. At even lower field  $(\delta =$ 10.31 ppm), a doublet could be attributed to a proton directly linked to the central macrocycle (by comparison, the protons directly linked to the macrocycle of the "ortho" and "para" isomers of tetraphenyl-carbo-benzenes C<sub>18</sub>Ph<sub>4</sub>H<sub>2</sub> resonate at  $\delta =$ 9.70 and 9.87 ppm, respectively).<sup>[11]</sup> This proton is actually coupled with another proton that resonates as a doublet at the opposite side of the spec-



Scheme 6. A priori possible structures for dihydro-*carbo*-benzene **5** (Scheme 3) on the basis of crude MS and <sup>1</sup>H NMR spectroscopic data. Refined NMR spectroscopic analyses reduced the possibilities to the three *trans* isomers, and finally to isomer **5A** (or its mesomeric form **5A**').

trum ( $\delta = -3.46$  ppm). The coupling constant of  ${}^{3}J(H,H) =$ 13 Hz suggests the presence of a trans-disubstituted double bond, which would be compatible with the extreme shielding and deshielding of the -CH=CH- protons that reside outside and inside the macrocycle, respectively. Among the five regio- or stereoisomeric structures a priori possible for 5, the compatible structures were thus reduced to the three trans isomers 5A, 5B, and 5C (Scheme 6). Finally, <sup>1</sup>H NOESY experiments evidenced that the double bond is located between two phenyl-substituted vertices, and thus allowed to assign the structure of 5 to the isomer 5A, which features a trans-substituted but-2-ene edge. It is noteworthy that the resonance form 5A' suggested by standard mesomerism is thus forced to retain the transoid configuration of the corresponding butadiene edge of 5A, at least on the NMR spectroscopic timescale at RT (Scheme 6). Although both forms may be equally representative (see below), the structure of the product 5 is henceforth represented by the form 5A, which is more descriptive of the rigid trans/transoid geometry.

As in the cases of 1 and 4A (see above), accurate structural data could not be gained by X-ray diffraction analysis of crystals of 5A (see below). The structure of 5A and those of its isomers 5B–E were thus calculated at the B3PW91/6-31G\*\* level. All the *trans*-isomers 5A–C were found to be quasi-isoenergetic and exhibit a planar C<sub>18</sub> macrocycle. In contrast, very distorted nonplanar structures were calculated for the *cis*-isomers 5D and 5E, that are respectively 17.5 and 28.6 kcalmol<sup>-1</sup> higher in energy than 5A. The calculated bond lengths of the non-hydrogenated edges of the C<sub>18</sub> ring of 5A (only 0.2 kcalmol<sup>-1</sup> lower in energy than **5B** and **5C**) are comparable to those calculated for **1** at the same level (Figure 9 and Figure S4 in the Supporting Information). It is noteworthy that the three C–C bond lengths of the hydrogenated edge of **5A** are almost equal (1.397–1.399 Å), thereby suggesting that the Kekulètype resonance forms **5A** and **5A'** have identical weights (Scheme 6). This indicates that **5A** and **1** sustain the same perfect cyclic delocalization of their  $\pi_z$ -electron systems, and exhibit similar structural aromaticity. Likewise, the NICS values calculated at the B3PW91/6-31+G\*\* level at the geometrical center of the C<sub>18</sub> macrocycle are equal to NICS=-12.8 ppm for **5A** and NICS=-13.5 ppm for **1**,



Figure 9. Calculated structure of dihydro-*carbo*-benzene 5A at the B3PW91/6-31G\*\* level. Bond lengths given in Å, dihedral angles in degrees. For comparison with 1, see Figure S4 in the Supporting Information.

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thus showing that both *carbo*-benzenes and *trans*-dihydro*carbo*-benzenes exhibit similar magnetic aromaticity. In agreement with the Hückel rule, indeed, both the *carbo*benzene **1** and dihydro-*carbo*-benzene **5A** satisfy an  $18-\pi_z$ electron count over the planar C<sub>18</sub> macrocycle.

The similarity of the  $\pi$ -electron delocalization in the dihydro-carbo-benzene 5A and carbo-benzene 1 is also appraised by comparison of their absorption spectra. In the visible region, 5A indeed presents a strong absorption band at  $\lambda_{max} = 467 \text{ nm} (\epsilon = 107679 \text{ Lmol}^{-1} \text{ cm}^{-1})$  and weaker bands at 526 and 588 nm (Figure S1c in the Supporting Information), which may be related to the bands of 1 at 482 ( $\varepsilon =$ 222112 Lmol<sup>-1</sup>cm<sup>-1</sup>), 525 and 580 nm, respectively (Figure 2 and Figure S1a in the Supporting Information). The main absorption band of 5A is, however, blue-shifted with respect to 1, thereby suggesting a slightly weaker " $\pi$ -delocalization" through the  $sp^2$ -C- $sp^2$ -C bond of **5A** than through the sp-C-sp-C bond of 1, as crudely indicated, in the dynamic context, by their relative NICS values (NICS = -12.8 versus -13.5 ppm; see above). The  $\lambda_{\text{max}}$  value of **5A** is thoroughly reproduced at the TDB3PW91/6-31G\*\* level of theory by two transitions that occur at 470.1 nm (2.6377 eV, f=1.326) and 465.7 nm (2.6623 eV, f=1.898). The description of the corresponding third and fourth singlet excited states is however different from the one of 1 (|S<sub>3</sub>>=0.42|H–1 $\rightarrow$ L>+  $0.38 | H \rightarrow L+1 > -0.36 | H-1 \rightarrow L+1 >$ and  $|S_4>=0.46|$  $H-1\rightarrow L+1 > +0.30 | H-1\rightarrow L >$ ). Secondary excitations of much weaker oscillator strengths, which exhibit a larger discrepancy with the observed secondary bands, are also calculated (see Table S5 in the Supporting Information).

A complete NMR spectroscopic study of 5A, including COSY-45, <sup>1</sup>H-<sup>13</sup>C HSQC, and HMBC experiments, allowed us to assign all the <sup>1</sup>H signals and most of the <sup>13</sup>C signals. The complete attribution of the macrocyclic quaternary <sup>13</sup>C nuclei was, however, not possible due to the absence of long-range coupling  $({}^{4}J(C,H)$  were not detected at 500 MHz). The <sup>1</sup>H and <sup>13</sup>C chemical shifts of **5A** were thus calculated at the B3PW91/6-31+G\*\* level with the GIAO method, from the static optimized geometry (Figure 9) and using the same averaging method for nuclei that become equivalent at the experimental NMR spectroscopic timescale at room temperature as the one used for the carbobenzene 1.<sup>[15]</sup> The results are in good agreement with available experimental data and allowed us to refine the assignment of the <sup>13</sup>C chemical shifts of the C<sub>18</sub> macrocycle (see Figure S9 in the Supporting Information).

The dihydro-*carbo*-benzene **5A** spontaneously crystallizes by evaporation of solutions in most organic solvents and mixtures thereof to give very thin needles, which did not appear suitable for X-ray diffraction analysis. The shape of these microcrystals could, however, be observed by SEM, after deposition on an aluminum support and coating with a conducing platinum film (Figure 10). The needles were found to be several hundreds of micrometers long, with a diameter of 15–20  $\mu$ m. Most of them exhibited a hexagonal section, and some of them were found to be tubular. Crystallization of organic compounds in tubular forms is actually





Figure 10. SEM images of crystals of dihydro-*carbo*-benzene 5A, showing long needles of regular hexagonal section (left), with possible tubular shapes (right).

quite unusual.<sup>[23]</sup> The formation of such tubular auto-assemblies indeed generally requires very particular conditions (addition of surfactants,<sup>[24]</sup> liquid crystals,<sup>[25]</sup> or mixtures of solvents<sup>[26]</sup>). In the case of the dihydro-*carbo*-benzene **5A**, tubular architectures are formed in the absence of any template upon quick evaporation of various usual organic solvents.

To gain insights into the way the hexagonal hollow tubes are formed, TEM analysis was performed from a rapidly evaporated drop of a diluted solution of **5A** in chloroform. The TEM images evidenced a fast auto-organization of the dihydro-*carbo*-benzene molecules in sheets in which parallel alignments are visible (Figure 11a). This structural periodicity was confirmed by the presence and the spacing of diffraction spots in the picture generated by Fourier transform of the TEM image, thereby revealing that the alignments are spaced out by approximately 15.5 Å (Figure 11b). The interpretation of these alignments is addressed below.

After several unsuccessful attempts, the X-ray crystal structure of **5A** could finally be determined using the X-ray microsource on microcrystals deposited from a 9:1 CHCl<sub>3</sub>/ CH<sub>3</sub>CN solution (Figure 12, Table S1 in the Supporting Information). Due to the weak diffraction of the crystals and to a high disorder of two non-equivalent molecular motifs

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Figure 11. TEM image of dihydro-*carbo*-benzene **5A** (top), and corresponding Fourier transform (bottom) revealing the presence of long-range alignments with a periodicity of 15.5 Å.



Figure 12. Molecular view of the X-ray crystal structure of dihydrocarbo-benzene **5A**. Thermal ellipsoids drawn at the 50% probability level (for clarity, the hydrogen atoms are omitted). Space group:  $P2_1/n$ ,  $R_1 (I > 2\sigma(I)) = 0.0872$ ).

(Figure 13 and Figure S10 in the Supporting Information), the poor quality of the resolution prevents a detailed discussion of quantitative structural data. Nonetheless, inspection of disordered motif the less (Figure 12) confirms the general features of the calculated structure in the gas phase (Figure 9): quasi-planarity of the macrocycle, relative order of magnitude of the bond lengths, bond angles and torsion angles, and so on. The only noticeable difference is a slight bending of the planes of the anisyl substituents out of the plane of the macrocycle (by around 7° in the less disordered motif and by 3.5° in the most disordered one).

The macrocycles of  $\mathbf{5A}$  stack in columns, the axes of which

are the normals to their centroids and oriented along the unit-cell axis that corresponds to a=7.118 Å. They are constituted by the two types of alternating molecular motifs separated by approximately 3.56 Å (see the Supporting Information). This is the shortest distance ever observed between two C<sub>18</sub> *carbo*-meric macrocycles in the crystal state, and thus the first evidence of a weak  $\pi$ -stacking between such macrocycles. In the same series, for example, the stacked C<sub>18</sub> macrocycles of the *carbo*-benzene **1** were found separated by twice the distance (7.34 Å) through weak  $\pi$ -stacking with intercalated phenyl rings (see above). In contrast to all previous observations, no solvent is involved in the crystal packing of **5A**, neither inside the columns<sup>[5b,11]</sup> nor outside (as in the case of **1** described above).

In the same crystal of **5A**, the distance between two nearest columns is equal to 17.917 Å, and the distance between two next-nearest columns is very close to this value and equal to the length of the unit-cell edge b=18.865 Å (Figure 13). A set of tightly neighboring columns defines the plane of their parallel axes along the direction of *a*. Two series of such planes are thus defined: the series parallel to the *b* axis (in magenta in Figure 13), and the series parallel to the diagonal of the (*b*,*c*) rectangle (in blue in Figure 13). The two series are characterized by interplane distances of  $x=bc/(b^2+c^2)^{\frac{1}{2}}=16.0$  Å and y=c/2=15.2 Å, respectively. Both distances are very close (within a 3% error) to the periodicity of the alignments (15.5 Å) observed in the TEM image of **5A** (Figure 11).<sup>[27]</sup>



Figure 13. Wireframe view of the unit cell (monoclinic, Z=4) along the *a* axis, revealing the regular hexagonal columnar packing of macrocycles **5A**. The projected global disorder results from the superimposition of two types of alternating molecular motifs with different specific disorders along the columns. Two series of planes containing the axes of tightly neighboring columns (either nearest columns equidistant by 17.917 Å, or next-nearest columns equidistant by b=18.465 Å) are defined: the series parallel to the *b* axis (in magenta), and the series parallel to the diagonal of the (*b*,*c*) rectangle (in blue). Each series is characterized by an interplane distance  $x=bc/(b^2+c^2)^{\frac{1}{2}}=16.0$  Å and y=c/2=15.2 Å, respectively, which are very close to the periodicity of 15.5 Å of the TEM image of **5A** (Figure 11).

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Table 1. CV and SWV data for 1, 4A, and 5A in  $CH_2Cl_2$ , and corresponding energetic data in the gas phase calculated at the B3PW91/6-31G\*\* level of theory. Electrochemical conditions: supporting electrolyte:  $[nBu_4N][PF_6]$  (0.1 M); working electrode: Pt; reference electrode: saturated calomel electrode (SCE, 0.242 V versus the hydrogen electrode); scan rate 0.1 Vs<sup>-1</sup> unless otherwise noted.

	$E^{\mathrm{red}}_{\frac{1}{2}}\left[\mathrm{V} ight]^{\left[\mathrm{a} ight]}$	$\Delta E_{\rm p}^{\rm red}  [{ m mV}]^{[b]}$	Reduction $E_p^{red} [V]^{[c]}$	EA [eV] <sup>[d]</sup>	$\varepsilon_{ m LUMO} \ [eV]^{[e]}$	$E^{\mathrm{ox}}_{\scriptscriptstyle 1\!\!/_{\!\!2}} \left[\mathrm{V} ight]^{\!\left[\mathrm{a} ight]}$	$\Delta E_{\rm p}^{\rm ox}  [{ m mV}]^{[{ m b}]}$	Oxidation $E_{p}^{ox} [V]^{[c]}$	IP [eV] <sup>[f]</sup>	$\varepsilon_{ m HOMO}  [{ m eV}]^{[{ m g}]}$
1	$-0.77 \\ -1.19$	60 60	-1.70	1.997	-2.83433			0.90 <sup>[i]</sup>	5.841	-5.02975
$4A^{[h]}$	-0.78	58	$-1.07 \\ -1.27$	2.085	-2.90824			1.00	5.612	-4.80863
5A	-0.85	69	$-1.22 \\ -1.48$	1.907	-2.75597	0.92 <sup>[j]</sup>	68	1.16	5.718	-4.89913

[a] Half-wave potential. [b] Peak potential difference at  $v = 0.1 \text{ Vs}^{-1}$ . [c] Peak potential for irreversible electron transfer. [d] Adiabatic electron affinity. [e] LUMO eigenvalue in the neutral ground state. [f] Adiabatic ionization potential. [g] HOMO eigenvalue in the neutral ground state. [h] Electrochemical measurements performed on the mixture of the *cis* and *trans* isomers of **4A**, calculation performed on *trans*-**4A**. [i] The oxidized product deposited on the electrode. [j] The oxidation is irreversible at  $v = 0.1 \text{ Vs}^{-1}$  but becomes reversible at  $v = 1.0 \text{ Vs}^{-1}$  (see Figure S3 in the Supporting Information).

**Comparative study of the redox properties of the dianisyl***carbo*-chromophores 1, 4A, and 5A: The electrochemical properties of 1, 4A, and 5A were studied by cyclic voltammetry (CV) and square-wave voltammetry (SWV) in dichloromethane (Table 1). Each of them exhibits three reduction waves corresponding to one-electron transfers according the half-height widths of the SWV peaks (Figure S3 in the Supporting Information).

In all cases, the first reduction step is reversible and

occurs at similar potentials  $(E_{1_{h}}^{\text{red}} = -0.77 \text{ V} \text{ for } \mathbf{1}, -0.78 \text{ V}$ for  $\mathbf{4A}$ , and -0.85 V for  $\mathbf{5A}$ ). This suggests that this first reduction occurs at a common conjugated structural unit, and indeed the LUMO of 1, 4A, and 5A is spread out over the dibutatrienylacetylene (DBA) units substituted by the same pairs of anisyl, phenyl, and alkynyl substituents (Figure 14). Nevertheless, the first reduction potential  $E_{1_{k}}^{\text{red}}$  does not correlate with the LUMO eigenvalue  $(\varepsilon_{\text{LUMO}})$ , which, however, accurately varies as the calculated adiabatic electron affinity (EA) in the gas phase (EA = -1.1688)- 1.3146 eV, R=1:  $\varepsilon_{\rm LUMO}$ Table 1).

The second reduction step is reversible for **1** at  $E_{\frac{1}{2}}^{\text{red2}} =$ -1.19 V (Figure S3 in the Supporting Information) and irreversible for **4A** and **5A** at  $E_p^{\text{red2}} = -1.07$  and -1.22 V, respectively (Table 1). The corresponding electron transfer is anticipated to target the SOMOs of the intermediate cations, which, in a very crude approximation, might be regarded as the half-filled LUMOs of the neutral species. It is incidentally observed that  $-\varepsilon_{\rm LUMO}$  correlates increasingly (but not linearly) with  $E_{\rm p}^{\rm red2}$ , and finally that  $\varepsilon_{\rm LUMO}$  varies accurately as  $E_{\rm av}^{\rm red} = (E_{\rm p}^{\rm red1} + E_{\rm p}^{\rm red2})/2$  (in which  $E_{\rm p}^{\rm red1}$  is denoted as  $E_{\rm b}^{\rm red}$  in Table 1).<sup>[28]</sup> In spite of their electron-rich character, the three chromo-

In spite of their electron-rich character, the three chromophores 1, 4A, and 5A can thus undergo sequential reduction steps, the first one at least being reversible. Their oxidation is more difficult, and only the dihydro-*carbo*-benzene



Figure 14. Frontier and near-frontier orbitals of 1, trans-4A, and 5A at the B3PW91/6-31G\*\* level.

5A can be reversibly oxidized at  $E_{14}^{\text{ox}} = 0.92 \text{ V}$ , albeit at scan rates higher than  $1.0 \text{ V}\text{s}^{-1}$  (Figure S3 in the Supporting Information). The carbo-benzene and carbo-cyclohexadiene counterparts 1 and 4A exhibited one oxidation step at similar  $E_{\rm p}^{\rm ox}$  potentials of 0.90 and 1.00 V, respectively, but in the case of 1, the formation of a conductive film on the electrode was observed (Table 1). Although the HOMO eigenvalue  $\varepsilon_{\rm HOMO}$  varies as the adiabatic ionization potential (IP = $-1.029 \ \varepsilon_{\text{HOMO}} + 0.66873 \text{ eV}, R =$ 0.998: Table 1),  $E_{\rm p}^{\rm ox}$  does not properly correlate with  $\varepsilon_{\rm HOMO}$ . As in the case of  $E_{\rm p}^{\rm red1}$  versus  $\varepsilon_{\text{LUMO}}$  (see above), the odd correlation might be first explained by the influence of the solvent and temperature (the DFT cal-



Scheme 7. Summary of the versatile reactivity of [6]pericyclynediol **3** under reducing acidic conditions (SnCl<sub>2</sub>/ HCl) in diethyl ether at low temperature: in addition to the "classical" *carbo*-benzene **1**, the sub-reduced *carbo*-cyclohexadiene **4A** and the over-reduced dihydro-*carbo*-benzene **5A** are produced.

culations were performed in the gas phase, and total Gibbs free energies were not considered) or by a possible multiconfigurational character of the ionized species (and calculation at higher level would thus be required). Nevertheless, the redox flexibility of the *carbo*-chromophores **1**, **4A**, and **5A** is clearly indicated by both electrochemical measurements and theoretical calculations. It accounts a posteriori for the versatile outcome of the reduction of the pericyclynediol **3** (Scheme 3).

It is finally noteworthy that the HOMO and two LUMOs exhibit similar localization along the series (Figure 14), whereas the strict HOMO-LUMO gap increases in the order 4A < 5A < 1. As the formal  $\pi$  conjugation is less extended in 4A than in 1 and 5A, this observation reminds that the definition of  $\pi$  delocalization depends on the selected criterion, and the HOMO-LUMO gap is just one among other.

#### Conclusion

Under controlled conditions of temperature and time, reductive treatment of the hexaoxy-[6]pericyclynediol **3** with SnCl<sub>2</sub>/HCl in diethyl ether has been shown to produce two unprecedented  $C_{18}$  "*carbo*-chromophores" beside the initially targeted macro-aromatic *carbo*-benzene **1**: the sub-reduced non-macro-aromatic *carbo*-cyclohexadiene **4A** and the over-reduced macroaromatic dihydro-*carbo*-benzene **5A**. Whereas the former is an intermediate in the formation of **1**, the latter does not result from the reduction of **1**, and its *endo*-macrocyclic double bond should thus result from an early reduction of one of the triple bonds of **3** (Scheme 7). The structure and the spectroscopic, chromophoric, and

redox properties of these carbo-chromophores have been investigated in detail with the complementary tools of experimental measurements and theoretical calculations at the DFT level. Their intriguing properties (aromaticity, dichromism, crystallinity, columnar auto-assembling, redox flexibility, and so on) are promising indicators of possible applications. In particular, some of these properties could be attributed to the common DBA unit, and the synthesis and physicochemical studies of other DBA derivatives deserve further investigation. Finally, the strongly quadrupolar or pseudo-quadrupolar character induced by the anisyl substituents of 1, 4A, and 5A also encourages investigation of their nonlinear optical properties, and in particular their two-photon absorption (TPA) properties. Prior to TPA cross-section measurements, preliminary theoretical studies are in current progress. Results will be communicated in due course.

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[28] This observation is completely empirical. However, by using the equation  $\Delta G^i = -iFE_p^{\text{redi}}$  for the simply (i=1) and doubly (i=2) reduced species,  $E_{av}^{\text{red}}$  appears as the average one-electron reduction potential through one-electron and two-electron transfer processes,

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## **FULL PAPER**





and might thus be also be regarded as a rough measure of the anyway non-observable LUMO energy.

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