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Carbo-cyclohexadienes *vs. carbo*-benzenes: structure and conjugative properties†‡

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Ideally C_s-/C_{2v}-symmetric chromophores, constituted by two electro-active groups conjugated through the *carbo*-mer of the cyclohexa-1,3-diene core, are selectively prepared by the $SnCl_2$-mediated reduction of tailored hexaoxy-[6]pericyclynes: in the latter substrates, one of the 1,4-dioxybut-2-yne edges is "chemically locked" by two CF_3 substituents preventing complete reduction to the corresponding aromatic *carbo*-benzenic core, which is expected to be more "π-insulating" between the electro-active ends. The bis-trifluoromethylated *carbo*-cyclohexadiene products are also shown to be significantly stabilized with respect to their bis-phenylated analogues. Their structural (crystal X-ray diffraction analyses), spectroscopical (NMR and UV-vis spectra), physio-optical (dichromism in solution) and electrochemical (cyclic voltammograms) properties are compared on the basis of the electron-donating/electron-withdrawing nature of the substituents. These properties are also compared with those of their aromatic *carbo*-benzene and flexible *carbo*-*n*-butadiene counterparts.

Introduction

Until the recent past,[1] the chemistry of *carbo*-mers mainly focused on *carbo*-benzenes,[2] because of the stability, rigidity and π-electronic features anticipated to be associated with their unique aromatic structure,[3] as compared to those of acyclic fragments. Like the C_6 ring of benzene, the C_{18} macrocycle of *carbo*-benzenes **A** (Fig. 1) can be formally divided into two acyclic components relevant from both the viewpoints of experimental retro-synthesis[4] and theoretical aromaticity analysis.[5] While the ethylene and 1,3-butadiene components for benzene are stable molecules, the issue for their partial *carbo*-mers, dialkynylbutatriene (DAB) and di(alkynylbutatrienyl)-acetylene (DBA, *i.e.* the functionality of *carbo*-*n*-butadiene) components, was less obvious (Fig. 1).[6] Recently, generic acyclic DBA derivatives **B** were shown to be actually quite stable and could be studied in a systematic manner.[7] In passing, they were found to be much more sensitive than the *carbo*-benzene counterparts **A** to the effects of electro-active substituents on the maximum UV-vis absorption wavelength (Fig. 1: R = 4-X–C_6H_4, X = NO_2, CF_3, H, OMe, NR'_2…).[7b] Whereas the phenomenon was tentatively attributed to macrocyclic aromaticity ("macro-aromaticity") making the C_{18} ring of **A** quite π-independent from its substituents R, the same *carbo*-benzene ring, which is anyway three-times smaller and three-times less energetically aromatic than benzene,[3f] has at most a weak electrical insulating effect. Very recently, indeed, the single molecule conductance (SMC) of a functional *carbo*-benzene **A** (R = 4-NH_2–C_6H_4)[4] measured by STM techniques proved to be much higher than that of benzenoid or porphyrine parents of similar size (*ca.* 2 nm), and almost two orders of magnitude higher than the SMC of the acyclic DBA counterpart **B** (R = 4-NH_2–C_6H_4) (106 nS *vs.* 2.7 nS).[8] On the basis of NEGF-DFT-calculations, this SMC difference was correlated with the difference in conformational freedom between the rigid *carbo*-benzene **A** and the freely rotating DBA derivative **B** (Fig. 1). The stiffness of **A** is, however, also effective in the σ-cyclic and π-acyclic *carbo*-cyclohexadiene **C**, which is a rigid version of the non-macro-aromatic DBA **B**, thus locked in a cisoid conformation. Access to **C** (R = 4-NH_2–C_6H_4) would thus allow an appraisal of the role of the macro-aromaticity of the equally rigid parent **A** on conduction. More fundamentally, the *carbo*-cyclohexadiene **C** is also the closest realistic non-aromatic but cyclic reference for the *carbo*-benzene **A**, just as cyclohexadiene is for benzene.[9]

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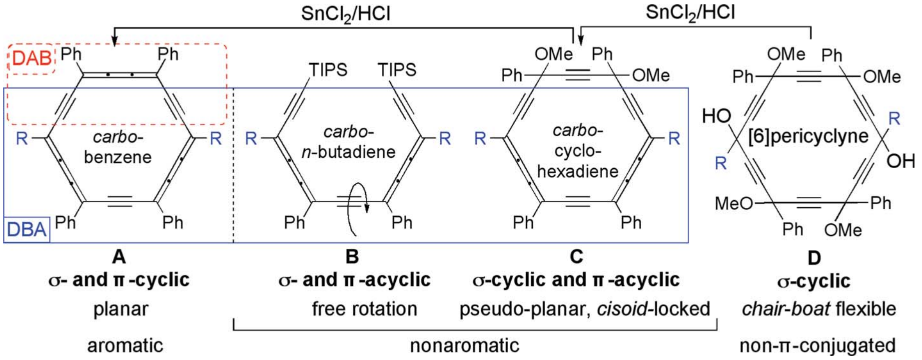


Fig. 1 The common DBA moiety in three types of *carbo*-meric molecules related to the *carbo*-benzene **A**, generated by reduction of the hexaoxy-[6]pericyclyne **D**, *via* the *carbo*-cyclohexadiene **C**. A complete **A**, **B**, **C** series is known for R = 4-MeO–C_6H_4.[10]

To date, a single example of *carbo*-cyclohexadiene has been reported:[10a] **C** (R = 4-MeO–C_6H_4) was incidentally isolated in low yield as a sub-reduced side product of the reductive aromatization of a hexaoxy-[6]pericyclyne[10b] **D** to the corresponding *carbo*-benzene **A**. The latter was also obtained by prolonged reductive treatment of the parent **C** (Fig. 1). Though it is quite sensitive in the solid state, this first *carbo*-cyclohexadiene was found to exhibit a persistent sharp turquoise blue-purple dichromism (or dichromatism) in solution.[10a] It thus appears in different colors to the human eye depending on the length of the optical path crossing the solution,[11] which is an unusual physio-optical property giving a further attractiveness to the class of chromophores **C**.

In order to guarantee the selective and systematic access to *carbo*-cyclohexadiene **C** with various types of substituents R, the control of the reduction step to preserve one of the 1,4-dioxybut-2-yne edges of the precursors **D** is the synthetic challenge addressed below.

Results and discussion

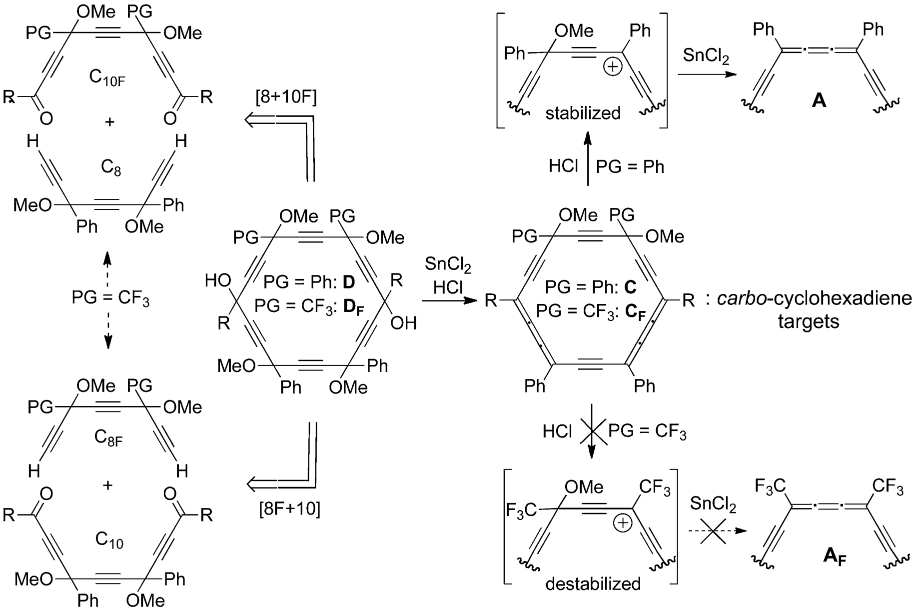
The sole known *carbo*-cyclohexadiene **C** (R = 4-MeO–C_6H_4) was obtained by serendipity at low temperature, thus indicating that the formation of the two first butatrienic edges of the *carbo*-benzene target **A** (R = 4-MeO–C_6H_4) was slightly faster than the formation of the third one.[10] Assuming that the mechanism of action of the reducing system $SnCl_2$/HCl starts with the formation of a bispropargylic carbenium from the corresponding carbinoxy vertex of the hexaoxy-[6]pericyclyne precursor **D** (Fig. 1),[12] the two anisyl-stabilized carbenium centers are likely to initially drive the formation of the butatrienic edges that are conjugated with the anisyl substituents R, as found in **C**. The phenyl-substituted carbinol ether vertices, though less reactive, remain, however, prone to dissociate under the operating acidic conditions, thus leading to **A** and making the partial reduction to **C** difficult to control.[10a,12] The selectivity for **C** should, however, be improved by increasing the difference in the mesomeric donor stabilization (+M effect) of the two types of carbenium centers. Ultimately, this should be improved by deliberately changing the two phenyl substituents for substituents exerting opposite mesomeric or inductive acceptor destabilization (–M or –I effect; the more or less protecting groups are denoted as PG in Scheme 1). Within this prospect, trifluoromethyl groups are ideal candidates:[13] it was indeed observed that the quite general method for the conversion of 1,4-dioxybut-2-yne derivatives to the corresponding butatrienes by treatment with $SnCl_2$/HCl is not compatible with CF_3 substituents.[6c] Two substituents PG = CF_3 at adjacent carbinoxy vertices of a hexaoxy-[6]pericyclyne $\mathbf{D_F}$ are therefore anticipated to freeze the reactivity of corresponding 1,4-dioxybut-2-yne edge towards reduction and thus optimize the selectivity for the partly reduced *carbo*-cyclohexadiene product $\mathbf{C_F}$ *vs.* the putative *carbo*-benzene $\mathbf{A_F}$ (Scheme 1).

The envisaged [8F + 10] and [8 + 10F] strategies to synthesise the bis-trifluoromethylated pericyclynic precursors $\mathbf{D_F}$ are inspired from a strategy previously used in the tetraphenylated series **D** and are based on a [8 + 10] cyclization step between a C_8 dinucleophile and a C_{10} dielectrophile, where the index F here refers to bis-trifluoromethylated synthons (Scheme 1). In spite of the recognized specificity of the chemistry of organofluorine compounds, both in terms of reactivity (due to extreme electronegativity and hardness) and purification (due to a high lipophilic character), the general strategic principles developed in the 1,4-diphenylbut-2-yne series[10a] are shown to be adaptable for the 1,4-bis(trifluoromethyl)but-2-yne series.

1. [8 + 10F] cyclization route to bis-trifluoromethylated hexaoxy-[6]pericyclynes

The fluorinated dialdehyde or diynone synthon C_{10F} was targeted through the known triyne intermediate **1** (Scheme 2).[6c] The latter was prepared in two steps from the diol **2** *via* the silylated triyne **3**, in 75% overall yield (in spite of its volatility) as a statistical mixture of *dl* and *meso* diastereoisomers, identified by two ^{19}F NMR singlet signals at −79.52 and −79.53 ppm. The mixture was not resolved before use as either the precursor of the C_{10F} synthon here, or the C_{8F} synthon in the [8F + 10] route (see Section 2).

Three C_{10F} synthons were prepared in two steps, starting with the addition of the dilithium salt of **1** to *p*-formaldehyde, *p*-anisaldehyde or benzaldehyde, giving the respective diols **4a**, **4b**, **4c** in 60–93% yields. Subsequent oxidation gave the



Scheme 1 [8 + 10F] and [8F + 10] strategies to synthesise bis-trifluoromethylated hexaoxy-[6]pericyclynes, envisaged as precursors for the selective synthesis of the corresponding *carbo*-cyclohexadienes.

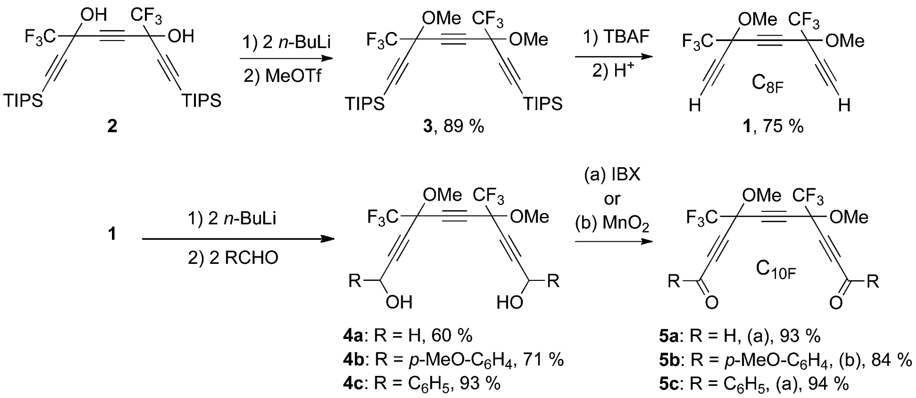
dialdehyde **5a** or diketones **5b** or **5c**, using either MnO_2 in dichloromethane (DCM) at room temperature or IBX in refluxing 1,2-dichloroethane (Scheme 2).

The C_{10F} synthons **5a–c** were then treated with the known dilithiated C_8 bis-terminal triyne **6** in THF at low temperature under quite diluted conditions (Scheme 3).[14] While the bis-tertiary [6]pericyclynediols **7b** and **7c** were obtained from the corresponding diketones in 40 and 18% yield, respectively, the bis-secondary [6]pericyclynediol **7a** could not be obtained from the dialdehyde **5a** (the final reaction mixture contained the starting triyne **6** and traces of linear oligomers). The CF_3 substituents, replacing the original phenyl substituents,[10a] are therefore responsible for the uncontrolled reactivity of the carbaldehyde groups in the γ position. The [6]pericyclynediol **7a** was also targeted as a possible precursor of the [6]pericyclynedione **8**, a putative pivotal reactant for the preparation of 1,10-disubstituted *carbo*-cyclohexadienes by addition of various nucleophiles to its keto groups (Scheme 3). A similar approach indeed proved to be efficient in the tetraphenyl series for the synthesis of *carbo*-benzenes through the tetraphenyl-[6]pericyclynedione analogue of **8**.[4,10a,14b]

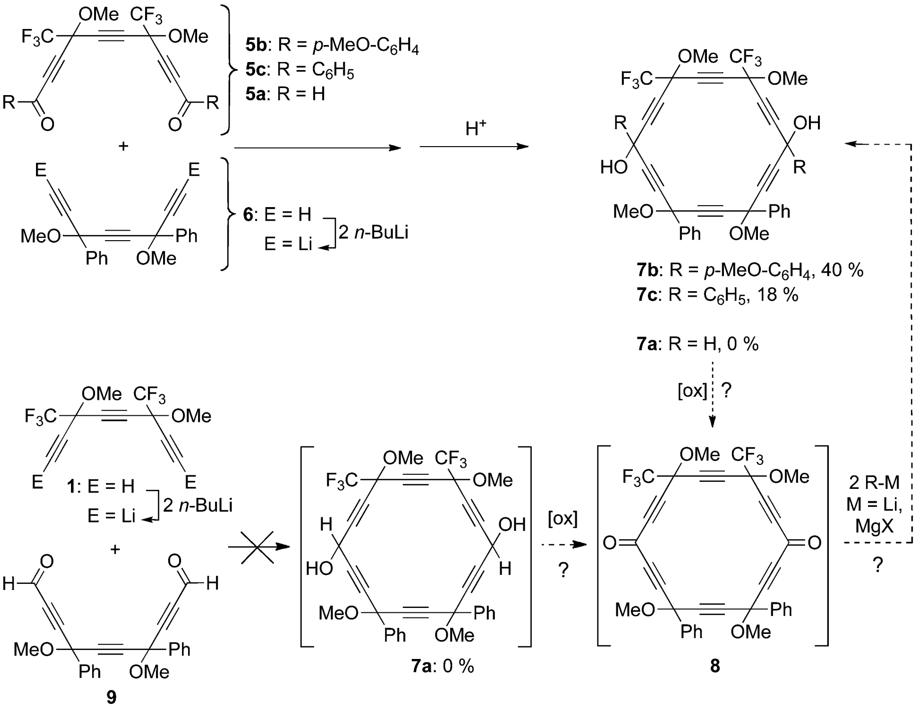
The synthesis of **7a** was also attempted through the alternative [8F + 10] strategy from the fluorinated triyne **1** as the C_{8F} dinucleophile, and the known dialdehyde **9** as the C_{10} dielectrophile,[14b] but without more success (Scheme 3).

2. [8F + 10] cyclization route to bis-trifluoromethylated hexaoxy-[6]pericyclynes

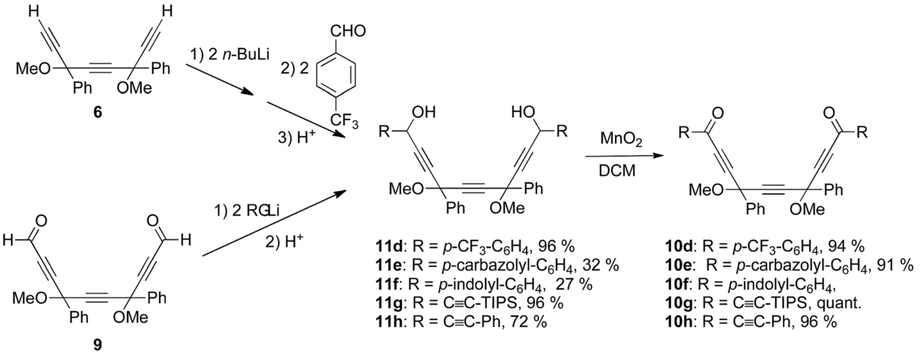
In spite of the intriguing failure of the [8F + 10] strategy from the C_{10} dialdehyde **9** (Section 1, Scheme 3), the same strategy was envisaged from C_{10} diketones. The triynediones **10d–h** were thus prepared using two alternative methods involving the bis-secondary diols **11d–h** as intermediates (Scheme 4). The first



Scheme 2 Synthesis of the dicarbonyl synthons C_{10F}, **5a–c**, *via* the bis-trifluoromethylated triyne **1**, also serving as the C8F synthon (see Fig. 1).



Scheme 3 The [8 + 10F] route to bis-trifluoromethylated bis-tertiary hexaoxy-[6]pericyclynediols **7b** and **7c**, and the attempted [8 + 10F] and [8F + 10] routes to the [6]pericyclynedione target **8** *via* the putative bis-secondary hexaoxy-[6]pericyclynediol **7a**.

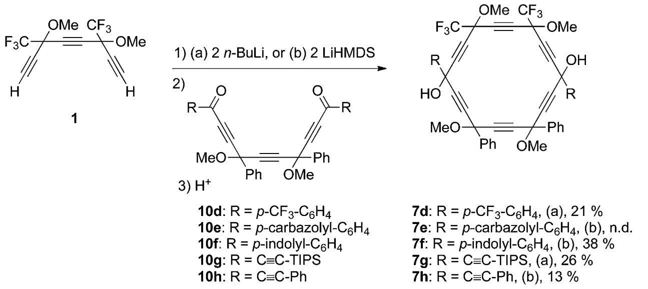


Scheme 4 Synthesis of the C_{10} diketone synthons to be involved in a [8F + 10] cyclization route to bis-trifluoromethylated [6]pericyclynes of type D_F (see Schemes 1 and 5).

method, recently described and consisting of a double addition of the bis-terminal triyne **6** to two equivalents of 4-(trifluoromethyl)benzaldehyde, gave the diol **11d** in 96% yield.[7b] The second method, involving the triynedial **9** as a dielectrophile towards various nucleophiles, led to the diols **11e–h**. The procedure, previously described for the preparation of **11g** in 96% yield from lithium triisopropylsilylacetylide,[4] was thus generalized to other nucleophiles, giving the diols **11e,f,h** in 27–72 % yield (Scheme 4). Isolation of the indolyl- and carbazolyl-substituted products **11e,f** required the aqueous treatment of the reaction medium at low temperature. The diols **11d–h** were then oxidized to the corresponding diketones **10d–h** using MnO_2 in DCM (Scheme 4).

The five C_{10} diketones **10d–h** were then involved in an [8F + 10] cyclization process with the same bis-trifluoromethylated dinucleophile **1**, the dilithium salt of which was prepared from either base, *n*-butyllithium or lithium hexamethyldisilazane (LiHMDS) (Scheme 5). In comparison to the use of a stoichiometric amount of *n*-butyllithium, which turned out to be inefficient in a few cases, the alternative use of four equivalents of LiHMDS afforded **7e,f,h**. While **7e** proved to be elusive upon chromatography, the [6]pericyclynediols **7d,f–h** were finally obtained in 13–38% yields, *i.e.* in the classical range of related [8 + 10] cyclization processes.[14b,15]

The [6]pericyclynediols **7d–h** were obtained as mixtures of diastereoisomers (20 in theory): this was evidenced by the extended ranges of resolved ^1H NMR signals of $C^*(R)OCH_3$



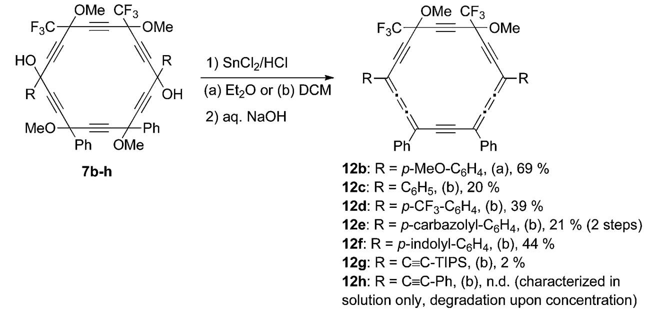
Scheme 5 [8F + 10] cyclization strategy from triynediones **10** to bis-trifluoromethylated hexaoxy-[6]pericyclynes **7** of type D_F (Scheme 3).

vertices (R = Ph, CF_3) and resolved ^{19}F NMR signals of C*(OMe) CF_3 vertices (around −79 ppm), induced by the rigid (cyclic) close stereochemical environment (in contrast, the 4-CF_3-C_6H_4 substituents of **7d**, remote from the stereogenic centers, resonate as a single broad ^{19}F singlet at −62.7 ppm: see Fig. 2).

Although the preparation of **7d–h** by the alternative [8 + 10F] route was not attempted, systematic comparison of the two routes will deserve special attention, in particular in view of elucidating the failure of both routes for the target **7a** and to allow the design of a suitable procedure for this target.

3. Reduction of bis-trifluoromethylated hexaoxy-[6] pericyclynes to *carbo*-cyclohexadienes

Reductive treatment of the [6]pericyclynediols **7b–h** with $SnCl_2$/HCl afforded the *carbo*-cyclohexadienes **12b–h** (Scheme 6). While the tetraaryl targets **12b–f** were readily obtained under classical conditions, the dialkynyl counterparts **12g,h** were more elusive. The reduction of **7g** was not selective, giving a mixture of undetermined products from which a minute



Scheme 6 The selective four-electron reduction of bis-trifluoromethylated hexaoxy-[6]pericyclynes to the corresponding conjugated *carbo*-cyclohexadienes.

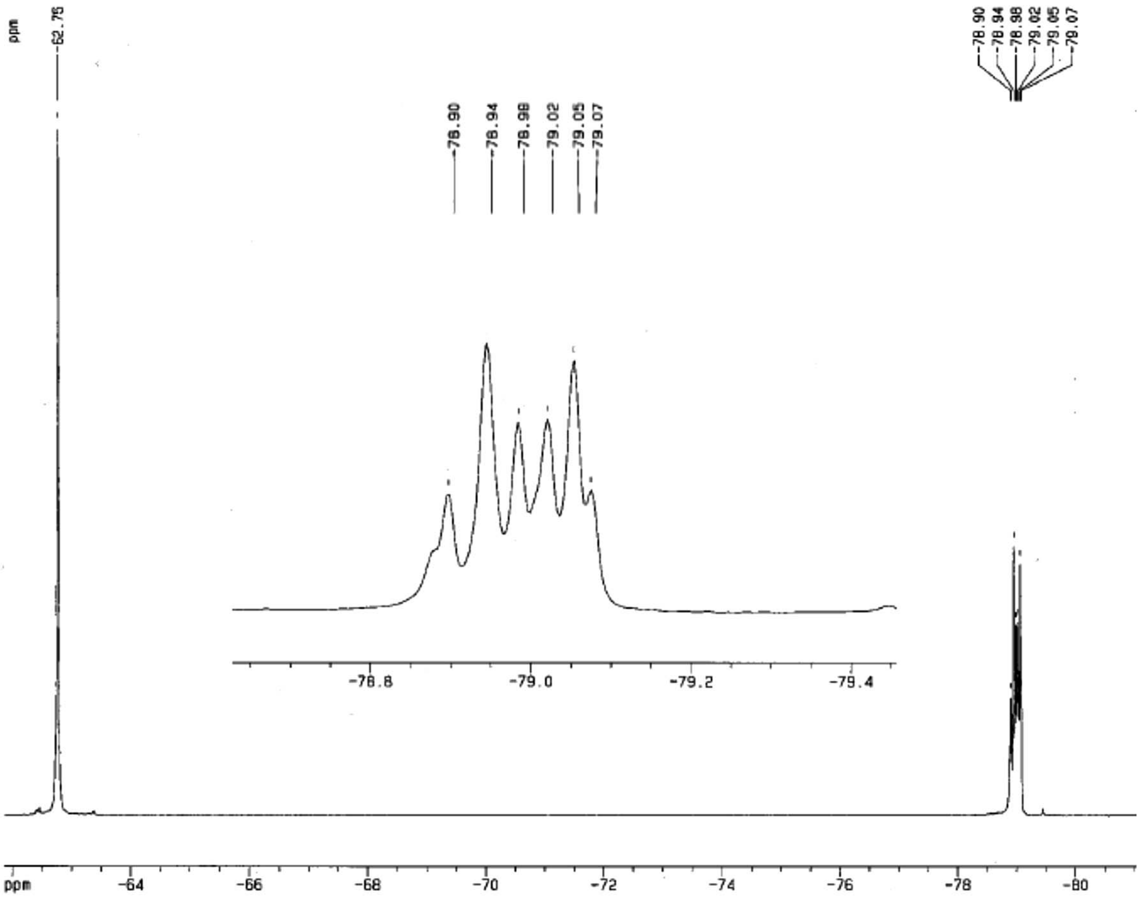


Fig. 2 ^{19}F NMR spectrum of the [6]pericyclynediol **7d** evidencing the occurrence of a diastereoisomeric mixture, 20 diastereoisomers in theory ($CDCl_3$, 282 MHz).

quantity of **12g** could be obtained. The reduction of **7h** turned out to be selective (with one main spot observed on TLC plates), but the product **12h** proved to be unstable in the solid state, giving instantly a black insoluble material when concentrated to dryness. The *carbo*-cyclohexadiene **12h** could, however, be characterized in solution, using a procedure avoiding the complete evaporation of the solvent.

The diastereoselectivity of the partial reduction process could not be determined from ^{1}H or ^{19}F NMR spectra of the crude materials because of a low resolution, likely due to traces of $SnCl_2$. After chromatography, however, the *carbo*-cyclohexadienes **12b** and **12d–h** were obtained as mixtures of *meso* (*cis*) and D/L (*trans*) isomers, identified by pairs of sharp ^{1}H NMR signals for the OCH_3 groups and pairs of sharp ^{19}F NMR signals for the CF_3 groups directly connected to the C_{18} macrocycle. For the tetraphenylated *carbo*-cyclohexadiene **12c**, single slightly broadened OC^1H_3 and $C^{19}F_3$ NMR signals were observed. In all cases, except in the case of **12h** (and, perhaps, **12c**), the mixture could be resolved by silicagel chromatography. ^{1}H and ^{19}F spectra of the two isomers of the representative example **12d** (without assignment) are shown in Fig. 3.

4. X-Ray crystallography of *carbo*-cyclohexadienes

Three of the bis-trifluoromethylated *carbo*-cyclohexadienes were obtained as crystalline solids.[16] X-Ray diffraction (XRD) analyses of selected crystals of **12b**, **12c** and **12d** confirmed the conjugated structure of the *carbo*-cyclohexadiene core. On the basis of experimental spectroscopic data only, it was not possible *a priori* to decipher whether the structure of the previously isolated tetraphenylated *carbo*-cyclohexadiene product was **C** (R = 4-MeO–C_6H_4), *i.e.* the core *carbo*-mer of the 1,3-cyclohexadiene parent, instead of the core *carbo*-mer of the 1,4-cyclohexadiene isomer (Fig. 1).[10a] The assignment was proposed on the basis of a comparison of the experimental UV-vis spectrum with the theoretical spectra of both the regioisomers, calculated at semi-empirical ZINDO or TD-DFT levels (only the conjugated butatriene edges of **C** give rise to the observed two intense bands spectrum: see Section 5).[10a] Since **12b** exhibits the same

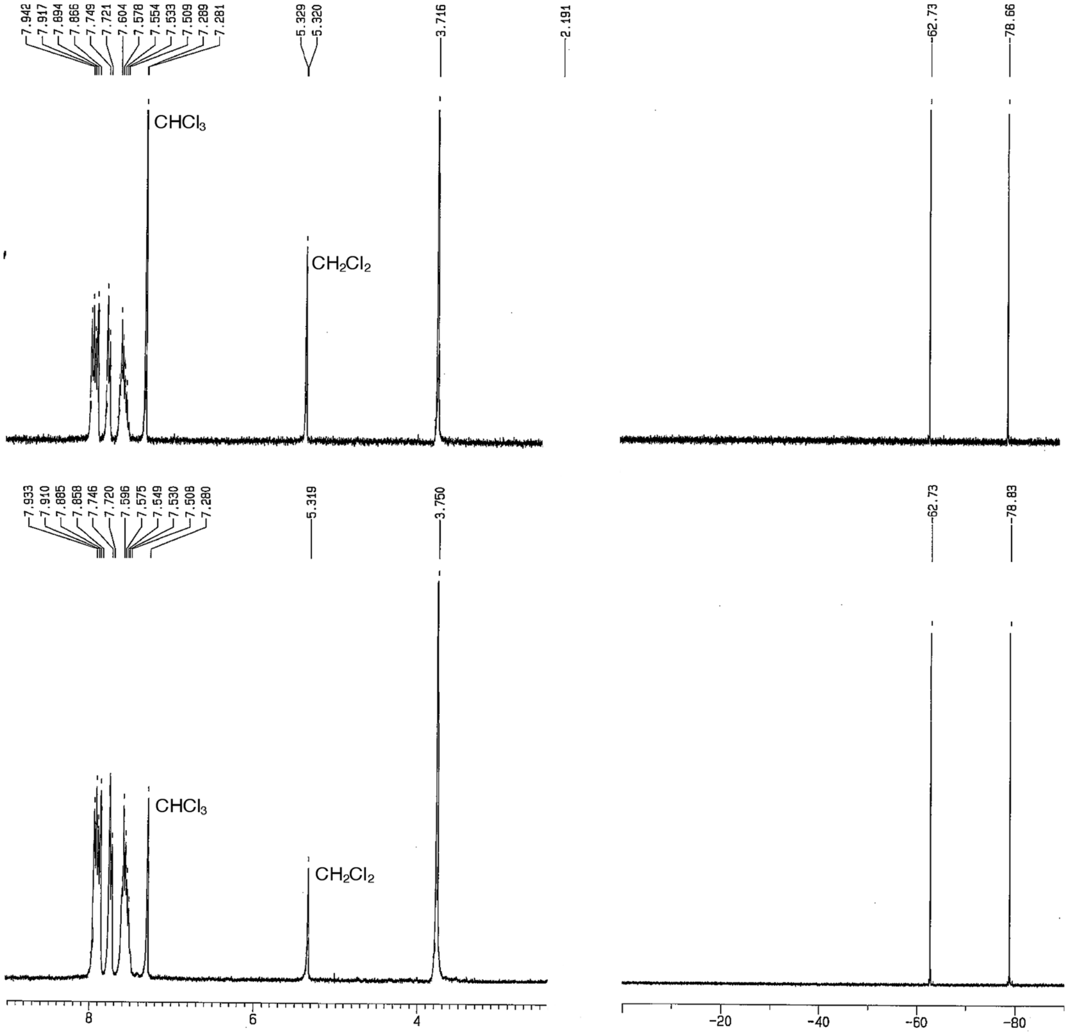


Fig. 3 ^{1}H NMR (300 MHz, left) and ^{19}F (282 MHz, right) NMR spectra of the resolved *meso* (*cis*) and D/L (*trans*) diastereoisomers of **12d**. Top: less polar (on TLC); bottom: more polar.

two-band UV-vis pattern, the XRD data of **12b** confirms the original assignment to **C** (R = 4-MeO–C_6H_4).

XRD analysis also revealed that the three *carbo*-cyclohexadiene crystals correspond to the *meso* (*cis*) stereoisomers **12b–d**, with similar geometrical features (Fig. 4). The C_{18} macrocycle is slightly distorted (maximum deviation from the mean plane: 0.43 Å for **12b**, 0.55 Å for **12c**, 0.23 Å for **12d**), with small torsion angles of the endocyclic DBA motif: 5.8°, 7.4° and 2.1° in **12b**, **12c** and **12d**, respectively. Nevertheless, in contrast to the quasi-planar *carbo*-benzenes of type **A** (Fig. 1), the butatriene and but-2-yne edges of the *carbo*-cyclohexadienes **12b–d** of type $\mathbf{C_F}$ are mesomerically non-equivalent and exhibit bond lengths close to those reported for the linear (σ-acyclic) DBA analogues of type **B**.[7] Indexing the DBA motif of **12b–d** as C7=C8=C9=C10(Ph)–C11≡C12–C13(Ph)=C14=C15=C16, the sequence of the bond lengths from C7 to C12 and from C16 to C11 reads (in Å): 1.355 (±0.010), 1.241 (±0.010), 1.356 (±0.010), 1.423 (±0.005), 1.196 (±0.005). The central and lateral Csp-Csp bonds exhibiting a significant difference in length (Δ = 0.045 Å) are therefore assigned to fixed triple and double bonds, respectively.

5. Absorption spectroscopy of *carbo*-cyclohexadienes

The *carbo*-cyclohexadienes **12** are highly chromophoric, possibly giving intense red (**12b,c**), blue (**12d–f,h**) or purple (**12g**) solutions in usual organic solvents. The electronic spectra of **12b–f,h** in diluted chloroform solutions are combined in Fig. 5 (the minute quantities and moderate stability of **12g** prevented full characterization). The spectra exhibit similar patterns, with two intense bands in the visible region (and a third intense band in the UV region due to carbazole and indole substituents for **12e** and **12f**, respectively). The same two-band pattern was previously observed for the tetraphenylated analogue **C** (R = 4-MeO–C_6H_4), theoretical spectra of which were also calculated at the TDDFT and ZINDO levels.[10a] These calculations were found to reproduce the observations, with high accuracy for the absolute transition energies (433 and 615 nm at the ZINDO level, *vs.* 437 and 602 nm for the experimental values) and definite agreement for the relative oscillator strengths (f = 1.60 at 433 nm, and f = 0.77 at 615 nm at the ZINDO level). The transitions were shown to involve the four orbitals of the Gouterman model (HOMO-1, HOMO, LUMO, LUMO+1), and one-electron excitations from the ground state S_0 to the first and third excited states S_1 and S_3, both centered on the conjugated DBA core.[10a] As the Ph or CF_3 substituents at the sp^3 carbon atoms of the *carbo*-cyclohexadiene ring are not π-conjugated with the DBA motif, the same interpretation can be inferred to apply in the $\mathbf{C_F}$ series. The variation of the maximum absorption wavelength ($\lambda_{\max}$) as a function of the substituents follows the same trend as the one previously observed for the σ-acyclic DBA derivatives of type **B**, with a slight general bathochromic shift for the present σ-cyclic series of type $\mathbf{C_F}$ (Fig. 1).[4,7] In this series, and by reference to the tetraphenylated dye **12c**, the largest bathochromic shifts are thus observed for the most donating anilinyl-type substituents of **12e** and **12f**. The still π-donating anisyl substituents of **12b** and extended phenylethynyl substituents of **12h** also induce higher $\lambda_{\max}$ values than the phenyl substituents of **12c**. In contrast, the electron-withdrawing *p*-trifluoromethylphenyl substituents of **12d** induce a small hypsochromic shift below the reference value of **12c** at 574 nm.

In the cyclic series $\mathbf{C_F}$, the molar extinction coefficient was found to vary from 9900 to 112900 L mol^{-1} cm^{-1}, the limit values being achieved for **12f** and **12d**, respectively. These values are in the same range as those previously reported in the acyclic series **B**.[7b] The fluorophore-substituted *carbo*-cyclohexadienes **12e** and **12f** were also found to be emissive at 427 (λ_{exc} = 243 nm) and 485 nm (λ_{exc} = 348 nm), respectively, namely at lower wavelengths than their σ-acyclic parents in the **B** series, emitting at around 500 nm.[4,7b]

Possible solvato-chromism in the *carbo*-cyclohexadiene series $\mathbf{C_F}$ was finally investigated for the selected tetrakistrifluoromethylated representative **12d**, which, contrary to its congeners, is soluble in a typical range of aprotic solvents, including pentane (see ESI†). Starting from pentane, after a first step of *ca* 10 nm, a quasi-negligible bathochromic shift with dielectric constant (ε_r) is observed, followed by another step of 4 nm for toluene, an aromatic solvent prone to bind with **12b** through specific π–π-stacking interactions: 416 and 568 nm in pentane (ε_r = 1.8), 423 and 578 nm in chloroform (ε_r = 4.8), 424 and 578 nm in THF (ε_r = 7.5), 427 and 582 nm in toluene (ε_r = 2.4).

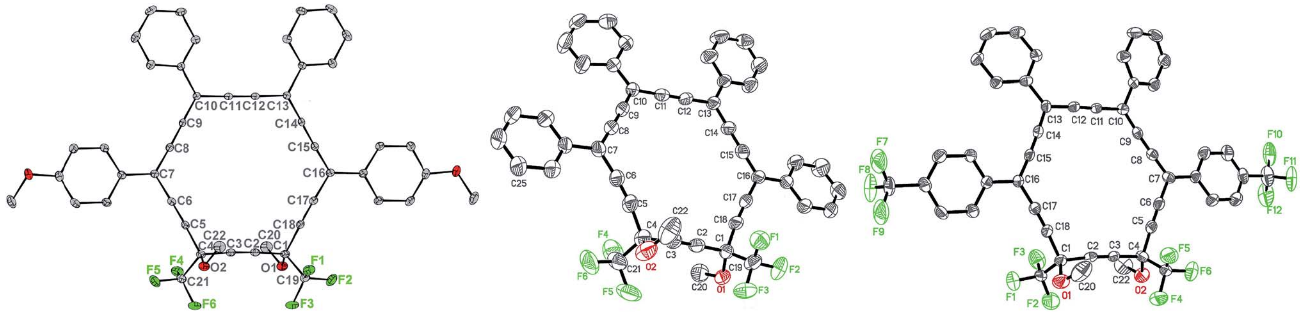


Fig. 4 Molecular views of the X-ray crystal structures of the *carbo*-cyclohexadienes **12b** (left), **12c** (middle), and **12d** (right) (Scheme 6). 50% probability level for the thermal ellipsoids. For clarity, all hydrogen atoms, disordered atoms and solvent molecules are omitted. DBA motifs: C7–C16.

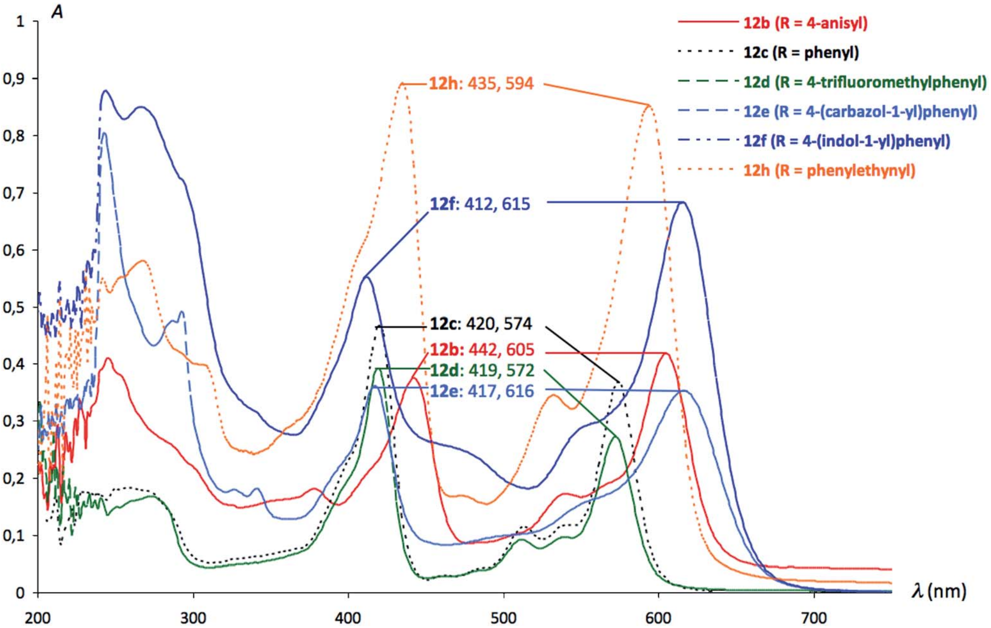


Fig. 5 Absorption spectra of the *carbo*-cyclohexadienes of type C_F, **12b–f,h** (in $CHCl_3$).

In a related context, as previously reported for a tetraphenyl-*carbo*-cyclohexadiene of type **C**,[10a] the bis-trifluoromethylated dyes of type $\mathbf{C_F}$ appear more or less dichromic in diluted solution.[11] In particular, the dianisyl-*carbo*-cyclohexadienes of types **C** (R = 4-MeO–C_6H_4) and $\mathbf{C_F}$ (**12b**) exhibit the same turquoise-blue/deep purple dichromism,[11] and almost superimposable UV-vis spectra, with two intense absorption bands at 437 and 602 nm for the **C** version, and at 442 and 605 nm for the $\mathbf{C_F}$ version **12b** (Fig. 6).

The dianisyl series (Fig. 1, R = 4-MeO–C_6H_4) is completed by two additional representatives **A** and **B**, where the central core is a rigid aromatic *carbo*-benzene ring in **A** and a flexible σ-acyclic *carbo*-*n*-butadiene unit in **B**. The latter possesses formally the same DBA π-conjugated system as in the σ-cyclic versions **C** or

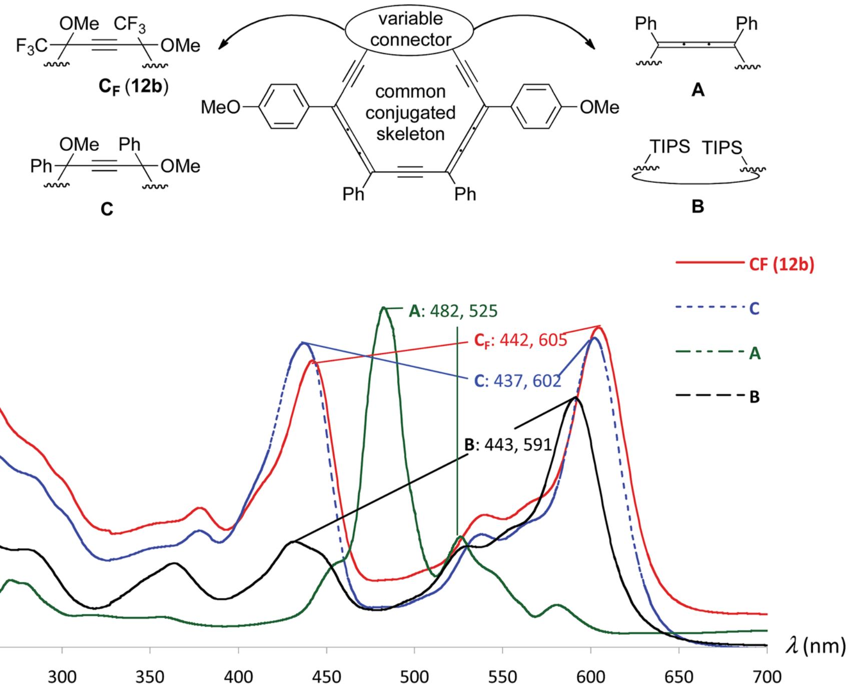


Fig. 6 UV-vis absorption spectra in $CHCl_3$ (bottom) of all the known dianisyl-substituted *carbo*-meric cores of the types **A**, **B**, **C** (Fig. 1, for R = 4-MeO–C_6H_4) and $\mathbf{C_F}$ (= **12b**) (top).

C_F (**12b**) and exhibits also a two-band absorption spectrum, with similar absorption wavelengths at 443 and 591 nm but with markedly different respective intensities (these intensities are similar in **C** and **C_F**). This difference is attributed to the much greater flexibility of the DBA motif in **B** by comparison to **C** and **C_F**. TDD-DFT or ZINDO calculations of the absorption spectra in the free-rotating series **B** would thus be much more challenging than in the locked series **C**, **C_F** or **A** (see above),[10a] as they would require full conformational analysis before relevant averaging. The effect of the cisoid-locked conformation of the DBA motif in **C** and **C_F** (**12b**) is thus dramatic, resulting, in particular, in a much weaker dichromism of the freely rotating *carbo-n*-butadiene **B**.

In contrast to the **B**, **C** and **C_F** representatives, the electronic spectrum of the quadrupolar dianisyl *carbo*-benzene **A** exhibits only one main absorption band (at 482 nm), as widely documented in the general *carbo*-benzene series.[2c,4,10a]

6. Electrochemistry of *carbo*-cyclohexadienes

The electrochemical properties of the *carbo*-cyclohexadienes of type **C_F** (excluding the poorly stable dialkynyl derivatives **12g** and **12h**) were investigated by square-wave (SW) and cyclic voltammetry (CV). The corresponding data are summarized in Table 1.

All the *carbo*-cyclohexadienes exhibit quasi-identical reduction behaviour, with three waves. The first one is reversible (except for **12e**) and occurs between −0.47 and – 0.67 V (the latter limit values being achieved for **12d** and **12b**, respectively). As previously observed in the *carbo-n*-butadiene series **B**, and as expected,[7b] the acceptor-substituted derivative **12d** of the **C_F** series (R = 4-CF_3–C_6H_4) is thus more prone to reduction. The first reduction potentials are, however, systematically higher (in algebraic value) in the *carbo*-cyclohexadiene series **C_F** than in the *carbo-n*-butadiene series **B** (italicized values in Table 1), likely because of the greater average stabilization of the anion through the optimally conjugated quasi-planar DBA motif of the **C_F** series. Another similarity between the series **C_F** and **B** is the result of the less donating character of the indolylphenyl and carbazolylphenyl substituents with respect to the anisyl substituent, the latter giving the smallest half-wave potential of the *carbo*-cyclohexadiene series ($E_{1/2} = -0.67$ V for **12b**).

In the oxidation process, the cations of the indolylphenyl- and carbazolylphenyl- substituted *carbo*-cyclohexadienes **12e** and **12f** were found to deposit on the electrode, giving electroactive films. In a complementary manner to what is observed in the reduction process, the *carbo*-cyclohexadienes **C_F** are less

Table 1 CV and SWV data for *carbo*-cyclohexadienes of type C_F, and comparison with the first reduction and oxidation potentials of the corresponding *carbo-n*-butadienes of type B (italicized values). Measurements performed at room temperature in DCM; supporting electrolyte: [*n*-Bu_4N][PF_6] (0.1 M); working electrode: Pt; reference electrode: saturated calomel electrode (SCE, 0.242 V *vs.* the hydrogen electrode); scan rate: 0.2 V s^{-1} unless otherwise noted

	Reductions				Oxidations			
	First reduction **C** series		First reduction **B** series[4,7b]	Other reductions **C** series[d]	First oxidation **C** series		First oxidation **B** series[4,7b]	Other oxidations **C** series[d]
Compound	$E_{1/2}$[a] (ΔE_p)[b]	RI_p[c]	$E_{1/2}$	E_p^{red}[e]	$E_{1/2}$[a] (ΔE_p)[b]	RI_p[c]	$E_{1/2}$ (ref. 4 and 7b)	E_p^{red}[e]
12b	−0.67 (0.06)[f]	1.00	−0.88	−0.95 −1.18 −1.44[j] −1.52[j] −1.61[j]	1.12 (0.09)[g]	0.86	0.95	1.68[h] 1.90
12c	−0.61 (0.06)	0.94	−0.80	−0.88 −1.07 −1.57[i]	1.33 (0.06)	1.05	0.95	1.60[g]
12d	−0.47 (0.06)	0.96	−0.65	−0.69[k] −1.84	1.54[h] irr.	— —	1.31	1.86
12e	−0.59irr.	—	−0.75	−0.80[l] −1.00 −1.44[j] −1.73[j]	1.21[h,i] irr.	—	1.06	1.42 1.68
12f	−0.60 (0.06)	1.17	−0.75	−0.85 −1.00 −1.43[j] −1.74[j]	1.17[h,i] irr.	—	1.04	1.60

[a] Half wave potential $E_{1/2} = (E_p^{red} + E_p^{ox})/2$, in V/SCE. [b] Separation between the two peak potentials: $\Delta E_p = |E_p^{red} - E_p^{ox}|$, in V. [c] Peak current ratio $RI_p = |I_p^{ox}/I_p^{red}|$. [d] Irreversible unless otherwise noted. [e] E_p values measured from CV in V/SCE. [f] Scan rate: 0.1 V s^{-1}. [g] Scan rate: 0.5 V s^{-1}. [h] After the first oxidation, a product deposited on the electrode. [i] Formation of an electroactive deposit observed. [j] Potentials obtained from SWV voltammograms. [k] Reversible couple: $E_{1/2} = -0.69$ V/SCE, $\Delta E_p = 0.07$ V, $RI_p = 0.92$. [l] Shoulder of low intensity, which could possibly correspond to an adsorbed product.

prone to oxidation than the *carbo*-*n*-butadiene counterparts **B** (italicized values in Table 1). Only the first oxidation waves of the dianisyl- and diphenyl-substituted derivatives **12b** and **12c** are reversible, with the most π-donating group, R = 4-MeO–C_6H_4, giving the lowest potential of the series ($E_{1/2}$ = +1.12 V for **12b**). In contrast, the most electron-withdrawing group, R = 4-CF_3–C_6H_4, induces the highest first oxidation potential at 1.54 V for **12d**. The quite high first oxidation potentials in the $\mathbf{C_F}$ series make the results difficult to interpret (due to the close oxidation wave of the solvent), but can be correlated to the corresponding low first reduction potentials: following a general trend, molecules that are readily reduced are not easily oxidized.

Conclusion

Since the incidental isolation of the first example of *carbo*-cyclohexadiene resulting from a partial reduction of a [6]pericyclyne,[10a] the introduction of a trifluoromethyl group on two adjacent vertices of hexaoxy-[6]pericyclynes allowed the selective synthesis of conjugated *carbo*-cyclohexadienes. These bore various types of electroactive substituents at the 1,10 positions of the *endo*-macrocyclic DBA motif, with spectator phenyl substituents at the 4,7 positions. Whereas the tetraaryl bis-trifluoromethylated *carbo*-cyclohexadienes were found to be stable both in solution and in the solid state, two dialkynyldiphenyl counterparts appeared less stable. Moreover, the trifluoromethylated *carbo*-cyclohexadienes appear much more stable than their phenylated analogues, without modifying their chromophoric and spectroscopic properties, as evidenced in the anisyl-substituted series. The optical and electronic properties of this novel type of *carbo*-meric chromophore deserve systematic attention. In particular, as justified in the introduction, the dianilinyl derivative $\mathbf{C_F}$ (R = 4-NH_2–C_6H_4, Fig. 1) is currently being targeted for measurement of its single molecule conductance (SMC) and comparison with the *carbo*-benzene **A** (R = 4-NH_2–C_6H_4).[8] As neither the [8 + 10F] nor the [8F + 10] strategy proved to be compatible with the NH_2 substituents, further methodological improvements are required. In parallel, theoretical studies are being undertaken to bring out the specific, but subtle effects of the CF_3 substituents in the $\mathbf{C_F}$ series, with respect to the phenyl substituents in the **C** series.[10a,17]

Acknowledgements

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