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

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Ideally C1−/C2−-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 SnCl2-mediated reduction of tailored hexa-xy-[6]pericyclics: in the latter substrates, one of the 1,4-dioxybut-2-yn-3-ene edges is "chemically locked" by two CF3 substituents preventing complete reduction to the corresponding aromatic carbo-benzenic core, which is expected to be more "π-insulating" between the non-aromatic 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 properties 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,† the chemistry of carbo-mers mainly focused on carbo-benzenes,‡ because of the stability, rigidity and π-electronic features anticipated to be associated with their unique aromatic structure,§ as compared to those of acyclic fragments. Like the C6 ring of benzene, the C18 macrocycle of carbo-benzenes A (Fig. 1) can be formally divided into two acyclic components relevant from both the viewpoints of experimental retro-synthesis¶ and theoretical aromatic analysis.‖ While the ethylene and 1,3-butadiene components for benzene are stable molecules, the issue for their partial aromaticity makes the C18 ring of A quite π-independent from its substituents R, where R is the carbo-benzene ring, which is way smaller and times less energetically aromatic than benzene,¶¶ has at most a weak electrical insulating effect. Very recently, indeed, the single molecule conductance (SMC) of a functional carbo-benzene A (R = 4-NH2-C6H4)¶¶ 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-NH2-C6H4) (106 nS vs. 2.7 nS).§ 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-NH2-C6H4) 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.§
To date, a single example of carbo-cyclohexadiene has been reported.\textsuperscript{19} C (R = 4-MeO-C\textsubscript{6}H\textsubscript{4}) was incidentally isolated in low yield as a sub-reduced side product of the reductive aromatization of a hexa-oxy-[6]pericyclene\textsuperscript{10} 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.\textsuperscript{19} It thus appears in different colors to the human eye depending on the length of the optical path crossing the solution,\textsuperscript{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\textsubscript{6}H\textsubscript{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\textsubscript{6}H\textsubscript{4}) was slightly faster than the formation of the third one.\textsuperscript{19} Assuming that the mechanism of action of the reducing system SnCl\textsubscript{2}/HCl starts with the formation of a bispropargylic carbenium from the corresponding carboxy vertex of the hexa-oxy-[6]pericyclene precursor D (Fig. 1),\textsuperscript{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 carbinal 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.\textsuperscript{10c,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:\textsuperscript{13} it was indeed observed that the quite general method for the conversion of 1,4-dioxybut-2-yn derivatives to the corresponding butatrienes by treatment with SnCl\textsubscript{2}/HCl is not compatible with CF\textsubscript{3} substituents.\textsuperscript{4c} Two substituents PG = CF\textsubscript{3} at adjacent carboxy vertices of a hexa-oxy-[6]pericyclene D\textsubscript{F} are therefore anticipated to freeze the reactivity of corresponding 1,4-dioxybut-2-yn edge towards reduction and thus optimize the selectivity for the partly reduced carbo-cyclohexadiene product C\textsubscript{F} vs. the putative carbo-benzene A\textsubscript{F} (Scheme 1).

The envisaged [8F + 10] and [8 + 10F] strategies to synthesise the bis-trifluoromethylated pericyclenic precursors D\textsubscript{F} are inspired from a strategy previously used in the tetraphenylated series and are based on a [8 + 10] cyclization step between a C\textsubscript{8} dinucleophile and a C\textsubscript{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-yn series\textsuperscript{19} are shown to be adaptable for the 1,4-bis(trifluoromethyl)but-2-yn series.

1. [8 + 10F] cyclization route to bis-trifluoromethylated hexa-oxy-[6]pericyclenes

The fluorinated dialdehyde or diynone synthon C\textsubscript{10F} was targeted through the known triyne intermediate 1 (Scheme 2).\textsuperscript{4c} 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 \textsuperscript{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\textsubscript{10F} synthon here, or the C\textsubscript{8F} synthon in the [8F + 10] route (see Section 2).

Three C\textsubscript{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
dialdehyde 5a or diketones 5b or 5c, using either MnO2 in dichloromethane (DCM) at room temperature or IBX in refluxing 1,2-dichloroethane (Scheme 2).

The C10F synthons 5a–c were then treated with the known dilithiated C8 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 CF3 substituents, replacing the original phenyl substituents,10a are therefore responsible for the uncontrolled reactivity of the carbalddehyde 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 8.4,10b,14b

The synthesis of 7a was also attempted through the alternative [8F + 10] strategy from the fluorinated triyne 1 as the C8F dinucleophile, and the known dialdehyde 9 as the C10 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 C10 dialdehyde 9 (Section 1, Scheme 3), the same strategy was envisaged from C10 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
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 dielectric towards various nucleophiles, led to the diols 11e–h. The procedure, previously described for the preparation of 11g in 96% yield,7b 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 MnO2 in DCM (Scheme 4).

The five C10 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]pericyclenioldiols 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]pericyclendiols 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)OCH₃.
vertices (R = Ph, CF₃) and resolved ¹⁹F NMR signals of C*(OMe)CF₃ vertices (around −79 ppm), induced by the rigid (cyclic) close stereochemical environment (in contrast, the 4-CF₃-C₆H₄ substituents of 7d, remote from the stereogenic centers, resonate as a single broad ¹⁹F 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]pericyclynecarboC-centered rings 7b–h with SnCl₂/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

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**Scheme 5** [8F + 10] cyclization strategy from triynediones 10 to bis-trifluoromethylated hexaoxy-[6]pericyclynes 7 of type D₄ (Scheme 3).

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

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**Fig. 2** ¹⁹F NMR spectrum of the [6]pericyclynecarboC-centered rings 7d evidencing the occurrence of a diastereoisomeric mixture, 20 diastereoisomers in theory (CDCl₃, 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$_3$H$_3$ and C$_3$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. 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$_6$H$_4$), i.e. the core carbo-mer of the 1,3-cyclohexadiene isomer (Fig. 1). 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).

![Fig. 3](image-url) $^1$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-C6H4).

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 C18 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 C are mesomerically non-equivalent and exhibit bond lengths close to those reported for the linear (σ-acyclic) DBA analogues of type B. 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-C6H4), theoretical spectra of which were also calculated at the TDDFT and ZINDO levels. 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 S0 to the first and third excited states S1 and S2, both centered on the conjugated DBA core. As the Ph or CF3 substituents at the sp3 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 C8 series. The variation of the maximum absorption wavelength (λmax) 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 C. 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 λmax 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 C, 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. The fluorophore-substituted carbo-cyclohexadienes 12e and 12f were also found to be emissive at 427 (λexc = 433 nm) and 485 nm (λexc = 348 nm), respectively, namely at lower wavelengths than their σ-acyclic parents in the B series, emitting at around 500 nm.

Possible solvato-chromism in the carbo-cyclohexadiene series C was finally investigated for the selected tetrakistri-fluoromethylated representative 12d, which, contrary to its congeners, is soluble in a typical range of aprotic solvents, including pentane (see ES1†). Starting from pentane, after a first step of ca. 10 nm, a quasi-negligible bathochromic shift with dielectric constant (εr) 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 (εr = 1.8), 423 and 578 nm in chloroform (εr = 4.8), 424 and 578 nm in THF (εr = 7.5), 427 and 582 nm in toluene (εr = 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.
In a related context, as previously reported for a tetraphenyl-carbo-cyclohexadiene of type C₁₀₁⁰aba, the bis-trifluoromethylated dyes of type CF₁₂ appear more or less dichromic in diluted solution. In particular, the dianisyl-carbo-cyclohexadienes of types C₁₂b and CF₁₂b (12b) exhibit the same turquoise-blue/deep purple dichromism, 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 CF version 12b (Fig. 6).

The dianisyl series (Fig. 1, R = 4-MeO-C₆H₄) 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...
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), 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-buta-diene 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.

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, 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 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 12c 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 stable.

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.

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a Half wave potential E_1/2 = (E_{red} + E_{ox})/2, in V/SCE. b Separation between the two peak potentials: ∆E_p = |E_{red} - E_{ox}|, in V. c Peak current ratio R = |I_{red}/I_{ox}|. 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, ∆E_p = 0.07 V, R_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-C₆H₄, giving the lowest potential of the series (E½ = +1.12 V for 12b).

In contrast, the most electron-withdrawing group, R = 4-CF₃-C₆H₄, induces the highest first oxidation potential at 1.54 V for 12d. The quite high first oxidation potentials in the C₆ 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]pericycylene, the introduction of a trifluoromethyl group on two adjacent vertices of hexa-oxy-[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-macroyclic DBA motif, with spectator phenyl substituents at the 4,7 positions. Whereas the tetaaryl bis-trifluoromethylated carbo-cyclohexadienes were found to be stable both in solution and in the solid state, two dialkynylidiphenyl counterparts appeared less stable. Moreover, the tri-fluoromethylated 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 C₆ (R = 4-NH₂–C₆H₄, Fig. 1) is currently being targeted for measurement of its single molecule conductance (SMC) and comparison with the carbo-benzene A (R = 4-NH₂–C₆H₄). As neither the [8 + 10] nor the [8F + 10] strategy proved to be compatible with the NH₂ substituents, further methodological improvements are required. In parallel, theoretical studies are being undertaken to bring out the specific, but subtle effects of the CF₃ substituents in the C₆ series, with respect to the phenyl substituents in the C₆ series.

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**Notes and references**


9 Since the pioneering work of L. P. Hammett (L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, NewYork, 1940), the effects of substituents on benzene derivatives have been thoroughly investigated, in particular by comparison with cyclohexadienes, which were theoretically evidenced to be more sensitive to substituent effects than their...


11 Dichromism, or dichromatism, is a property of some materials or solutions, which makes them appear in two different colors to the human eye depending on the concentration of the absorbing dye and on the thickness of the traversed medium. For references, see: (a) H. Cartwright, J. Chem. Educ., 1986, 63, 984–987; (b) S. Kreft and M. Kreft, Naturwissenschaften, 2007, 94, 935–939; (c) J. P. Launay, unpublished report, Toulouse (private communication); (d) J. P. Launay, La vision des couleurs, “Regards Croisés” conference at the Interdisciplinary Doctoral Workshop 2014-2015 of the IUF on the theme “The color”, University of Toulouse, November 4, 2014.


16 (a) Crystallographic data for 12b: C₄₈H₃₀F₆O₄, M = 784.75, Monoclinic, space group C2/c, a = 13.07527(8) Å, b = 16.18867(10) Å, c = 19.01027(12) Å, β = 100.1002(6)°, V = 3961.57(4) Å³, Z = 4, crystal size: 0.15 × 0.15 × 0.25 mm³, 35692 reflections collected (3771 independent, Rint = 0.0213), 262 parameters, R1 [I > 2σ(I)] = 0.049, wR2 [all data] = 0.065, largest diff. peak and hole: 0.61 and −0.57 eÅ⁻³, CCDC 1003439; (b) crystallographic data for 12c: C₄₈H₂₆F₆O₂, CHCl₃, M = 980.04, Monoclinic, space group P2₁/c, a = 12.8182(16) Å, b = 35.815(5) Å, c = 9.7626(14) Å, β = 92.841(6)°, V = 4476.4(11) Å³, Z = 4, crystal size: 0.20 × 0.20 × 0.04 mm³, 59064 reflections collected (7551 independent, Rint = 0.1994), 653 parameters, 102 restraints, R1 [I > 2σ(I)] = 0.0829, wR2 [all data] = 0.2414, largest diff. peak and hole: 0.573 and −0.326 eÅ⁻³, CCDC 951896; (c) crystallographic data for 12d: C₄₈H₂₆F₆O₂, CH₂Cl₂, M = 809.59, Triclinic, P1, a = 12.5119(17) Å, b = 12.6648(17) Å, c = 14.9565(19) Å, α = 70.805(5)°, β = 66.621(5)°, γ = 67.665(5)°, V = 1967.5(5) Å³, Z = 2, crystal size: 0.20 × 0.10 × 0.04 mm³, 28934 reflections collected (7350 independent, Rint = 0.0906), 669 parameters, 489 restraints, R1 [I > 2σ(I)] = 0.0672, wR2 [all data] = 0.1983, largest diff. peak and hole: 0.212 and −0.314 eÅ⁻³, CCDC 951897.

17 H. Hamdani, C. Lepetit and R. Chauvin, unpublished results.