Chem Soc Rev

« Carbo-aromaticity » and novel carbo-aromatic compounds

Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-03-2015-000244.R1
Article Type:	Review Article
Date Submitted by the Author:	18-May-2015
Complete List of Authors:	Cocq, Kévin; Toulouse 3 University, Laboratoire de Chimie de Coordination du CNRS Lepetit, Christine; CNRS ; LCC (Laboratoire de Chimie de Coordination) Toulouse, France, UPR 8241 Maraval, Valérie; CNRS ; LCC (Laboratoire de Chimie de Coordination), Chauvin, Remi; Toulouse 3 University, Laboratoire de Chimie de Coordination

Revised CS-REV-03-2015-000244

« *Carbo*-aromaticity » and novel *carbo*-aromatic compounds

Kévin Cocq,[a,b] Christine Lepetit,[a,b] Valérie Maraval,*[a,b] and Remi Chauvin*[a,b]

[a] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4 (France)*

[b] *Université de Toulouse, UPS, ICT-FR 2599, 31062 Toulouse Cedex 9 (France)*

Fax: (+33)5 61 55 30 03

E-mail: valerie.maraval@lcc-toulouse.fr, chauvin@lcc-toulouse.fr

Keywords. *Alkynes - Aromaticity - Carbo-benzenes - Carbo-mers - Graphyne - Macrocycles*

Abstract.

While the concept of aromaticity is being more and more delineated, the category of « aromatic compounds » is being more and more expanded. This is illustrated by an introductory highlight of the various types of « aromaticity » previously invoked, and by a focus on the recently proposed « aromatic character » of the « two-membered rings » of the acetylene and butatriene molecules. This serves as a general foundation for the definition of « *carbo*-aromaticity », the relevance of which is surveyed through recent results in the synthetic, physical, and theoretical chemistry of *carbo*-mers and in particular macrocyclic-polycyclic representatives constituting a natural family of « novel aromatic compounds ». With respect to their parent molecules, *carbo*-mers are *constitutionally* defined as "carbon-enriched », and can also be *functionally* regarded as « π-electron-enriched ». This is exemplified by recent experimental and theoretical results on functional, aromatic, rigid, σ,π-macrocyclic *carbo*-benzene archetypes of various substitution patterns, with emphasis on the quadrupolar pattern. For the purpose of comparison, several types of non-aromatic references of *carbo*-benzenes are then considered, *i. e.* freely rotating σ,π-acyclic *carbo*-*n*-butadienes and flexible σ-cyclic, π-acyclic *carbo*-cyclohexadienes, and to « pro-aromatic » congeners, *i. e.* rigid σ,π-macrocyclic *carbo*-quinoids. It is shown that functional *carbo*-mers are entering the field of "molecular materials" for properties such as linear or nonlinear optical properties (*e. g.* dichromism and two-photon absorption) and single molecule conductivity. Since total or partial *carbo*-mers of aromatic carbon-allotropes of infinite size such as graphene (graphynes and graphdiynes) and graphite ("graphitynes") have long been addressed at the theoretical or conceptual level, recent predictive advances on the electrical, optical and mechanical properties of such *carbo*-materials are surveyed. Very preliminary experimental results on a *carbo*-benzenoid fragment are finally disclosed.

1. Introduction

Like other key chemical concepts such as electronegativity,[1] or chirality,[2] aromaticity remains defined in a fuzzy manner insofar quantitative-comparative aspects are concerned.[3] Whereas many alternative numerical scales have been proposed for all the three concepts, both the definition and quantification of aromaticity have given rise to the most lively debates over the last 30 years.[3] Since Katritzky's factorial analysis,[4] aromaticity has been considered as a three-headed Janus-like amtrivalent concept refereing to the energetic,[5] structural,[6] and magnetic criteria,[7] more recently complemented by the electronic delocalization criterion.[8] Nevertheless, the corresponding properties happen to be correlated over particular sets of molecules as a result of some unified heuristic feature of « substantial aromaticity ».[9] According to the IUPAC Gold Book, aromaticity remains defined on a quite complex ground,[10] but in the spirit of Pauling's definition of electronegativity (« *the power of an atom to attract electrons to itself* »),[1a,11] a first-level qualitative definition can be expressed as « *the tendency to resist the loss of the cyclic character under the constraint of external perturbations* ».[12] Following this semantics, aromaticity is thus measured by the theoretical minimum energy sufficient to just delete the cyclic character of a ring without changing any other characteristic of the molecule. In spite of the *a priori* fictitious nature of the process, the corresponding exact definition, based on spectral graph theory (the mathematical basis of the Hückel Molecular Orbital (HMO) method), has long ago been proposed simultaneously by Aihara,[13] and Gutman, Milun and Trinajstic.[14] The so-defined « topological resonance energy » (TRE) is thus the conceptual limit for which all the other resonance or aromatic stabilization energies stand as approximates.[9] Because of the abstract and complex mathematical nature of the definition, TRE has been rarely used in the chemist community for the purpose of comparing the aromatic character of molecules. Very recently, however, the chemical significance of TRE has been unveiled: TRE is thus equal to half the opposite of the enthalpy of the *twist*ing head-to-tail *r*ing-*o*pening, *r*ing-*c*losing metathesis (*twist*-® = « *twist*-

*roc*king » reaction) of the ring of interest (Fig. 1).[15] The « vertical TRE » values (corresponding to the original purely topological definition of TRE) are readily available from standard HMO softwares for any hydrocarbon ring, like those of benzene derivatives, or any heterocycle.[16] Using the freeware HuLiS program,[17] implementing the Van-Catledge Hückel parameters,[18] the method can be applied to Nozoe's non-benzenoid aromatic paradigms, namely tropone and tropolone:[19] it is thus checked that both oxygenated compounds are less aromatic than benzene (TRE = 0.273 β^0) and the tropylium cation (TRE = 0.225 β^0),[10] and that tropolone is slightly more aromatic than tropone (TRE = 0.172 β^0 *vs* 0.170 β^0). In the search for novel non-benzenoid aromatic compounds, the topological approach allows the natural generalization of the TRE measure to the degenerate [n]annulene for n = 2, i.e. to acetylene and more generally to conjugated alkynes. The TRE acyclic reference of acetylene is thus the Möbius cyclobutadiene, an unknown compound that is however fully defined by a real Hamiltonian operator. Acetylene thus appears to be more than four times « more aromatic » than benzene (TRE = 1.172 β^0 *vs* 0.273 β^0), thus corroborating the necessary condition for a relevant aromaticity measure that the smaller the 4n+2-electron ring, the higher its energetic aromaticity.[6a] The generalization of the chemical interpretation of TRE to polycyclic compounds is being currently investigated, but the most straightforward issue applies to cyclically π-conjugated cyclynes and cyclenynes where the local aromatic character of the macrocycle is deduced by fixing the formal *sp*C-*sp*C two-membered rings through a double resonance integral value ($\beta_{sp\text{-}sp} = 2\ \beta^0$).[9] This is particularly relevant for highly symmetrical cyclenynes like *carbo*-meric rings. *Carbo*-benzene can thus be regarded as a heptacycle made of one C_{18} macrocycle and six C_2 microcycles, but the partial (or local) aromatic character of the C_{18} ring is readily obtained as the enthalpy of a twist-rocking chemical equation (Fig. 1, *bottom*): the acyclic reference of the *carbo*-mer of benzene is thus the *carbo*-mer of the acyclic reference of benzene, *i.e.* the *carbo*-mer of the Möbius

[12]annulene. Moreover, while the size of the C_6 benzene ring is *ca* one third of the size of the C_{18} *carbo*-benzene ring, the TRE value of the latter is also one third of the TRE value of the former ($0.089\ \beta^0$ *vs* $0.273\ \beta^0$).[9] It is also noteworthy that the *carbo*-benzene ring is slightly more aromatic than the [18]annulene ring (TRE = $0.089\ \beta^0$ *vs* $0.088\ \beta^0$).[10] Finally, using Aihara's definition of local aromaticity of a ring in a polycycle,[20] the aromaticity of the C_2 « microcycles » of *carbo*-benzene is found significantly lower than the aromaticity of acetylene (TRE = $0.908\ \beta^0$ *vs* $1.172\ \beta^0$).[10]

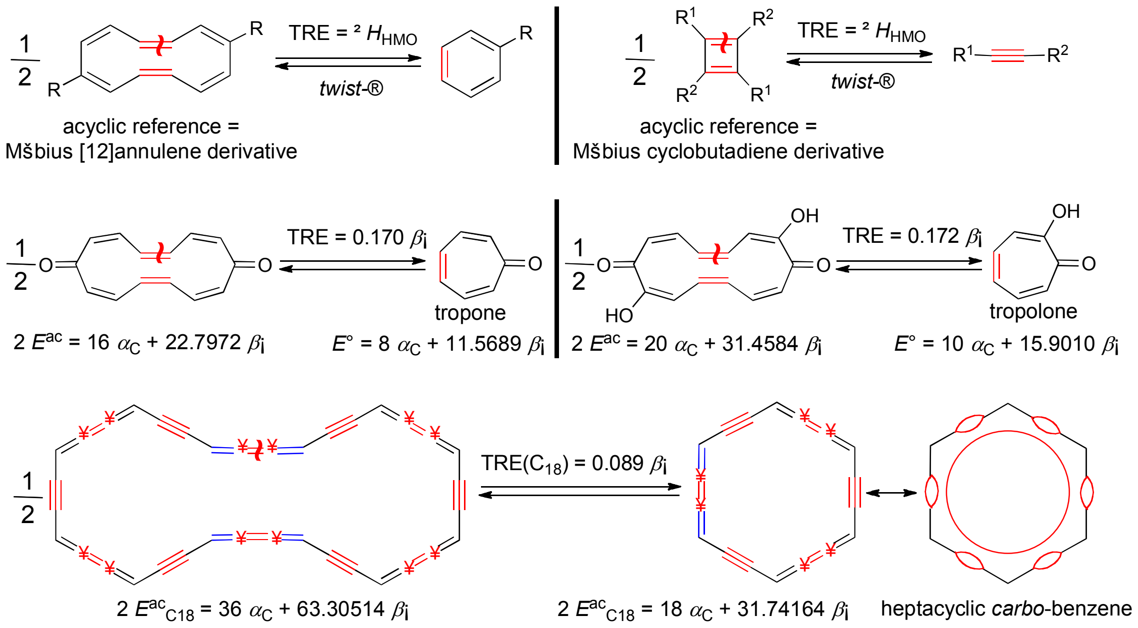


Fig. 1. Chemical equation of TRE ("twist-®" reaction) for benzene derivatives (*top left*), acetylene derivatives (*top right*), tropone (*middle left*), tropolone (*middle right*) and *carbo*-benzene (*bottom*). The tilde symbol ~ denotes the twist of the Möbius strip embedding the cyclic π system. β^0 denotes the HMO resonance integral of all the individual C-C π-bonds, and α_X the Coulomb integral of atoms of type X. The Van-Catledge Hückel parameters are used: $\alpha_C = 0$, $\alpha_{O=} = 0.97\ \beta^0$, $\alpha_{HO-} = 0.66\ \beta^0$, $\beta_{O=C} = 1.06\ \beta^0$, $\beta_{HO-C} = 0.66\ \beta^0$. For R = H, TRE(benzene) = $0.273\ \beta^0$; for $R^1 = R^2 = H$, TRE(acetylene) = $1.172\ \beta^0$.

In spite of the rigorous TRE rationale, the endless richness of the aromaticity concept is illustrated by the numerous definitions of aromaticity-related structural types far beyond the benzene paradigm, and beyond the basic features of aromaticity and anti-aromaticity *vs* non-aromaticity. Apart from the classical criteria of topological, structural, energetic, magnetic or electronic aromaticity, and besides the dual concepts of global *vs* local aromaticity,[21] peripheral *vs* spherical aromaticity,[22] in-plane *vs* out-of-plane aromaticity,[23] Hückel *vs* Möbius aromaticity,[24] or absolute *vs* compactness aromaticity,[25] the following terminologies were coined by resorting to many kinds of prefixes: pseudo-aromaticity,[26] iso-aromaticity,[27] super-aromaticity,[28] hyper-aromaticity,[29] homo-aromaticity,[30] hetero-aromaticity,[31] spiro-aromaticity,[32] pro-aromaticity,[33] metallo-aromaticity,[34] chelato-aromaticity,[35] quasi-aromaticity,[36] equi-aromaticity,[37] macro-aromaticity,[38] etc… Within this context, the title term « *carbo*-aromaticity » is here coined as a natural heading for the following review on recent advances in the chemistry of *carbo*-benzene derivatives, within the more general context of the chemistry of *carbo*-mers.[39] The most exemplified *carbo*-benzene series is first presented, the earliest representatives having been targeted for studying specific effects of *carbo*-meric expansion on aromaticity by comparison with *non-expanded* parents. As aromaticity itself is evaluated by comparison with *non-aromatic* references, the scope of the review is twofold: compare *carbo*-benzenic *carbo*-aromatics with both (i) their non-expanded benzenic parents and (ii) their *carbo*-meric "non-aromatic" references, namely σ-cyclic *carbo*-cyclohexadienes and σ,π-acyclic *carbo*-*n*-butadienes. Thanks to the above-proposed generalization of the definition of aromaticity to triple bonds, the latter references can actually also be themselves considered as "aromatic".

2. Monocyclic *carbo*-mers: *carbo*-benzenes and their π-acyclic references

2.1. Non- or partly substituted *carbo*-benzenes

The most exemplified series of *carbo*-mers consists in *carbo*-benzenes (*i. e.* ring *carbo*-mer derivatives of benzene), the unsubstituted representative $C_{18}H_6$ **1a**, originally targeted in 1995,[40] remaining experimentally unknown. Partly substituted *carbo*-benzenes have thus been described as stable molecules, and the less substituted representative is the is the octupolar triaryl-*carbo*-benzene **1b** containing three alternate CH vertices at the C_{18} macrocycle (Fig. 2): it was reported by Ueda, Kuwatani *et al.*, simultaneously to the first examples of *carbo*-benzenes in the hexasubstituted series,[41] the syntheses of which had been reviewed elsewhere.[42] Tetrasubstituted representatives have also been reported in both the dipolar series (**1c** and **1d**) and quadrupolar series (**1e**) (Scheme 1),[43] the respective synthetic strategies depending on the position of the unsubstituted vertices on the C_{18} macrocycle. All the *carbo*-benzenes known to date have actually been prepared by reductive aromatization of hexaoxy[6]pericyclynic precursors of type **2**,[44] themselves obtained through a macrocyclization step adapted to each kind of substitution profile of the targets.

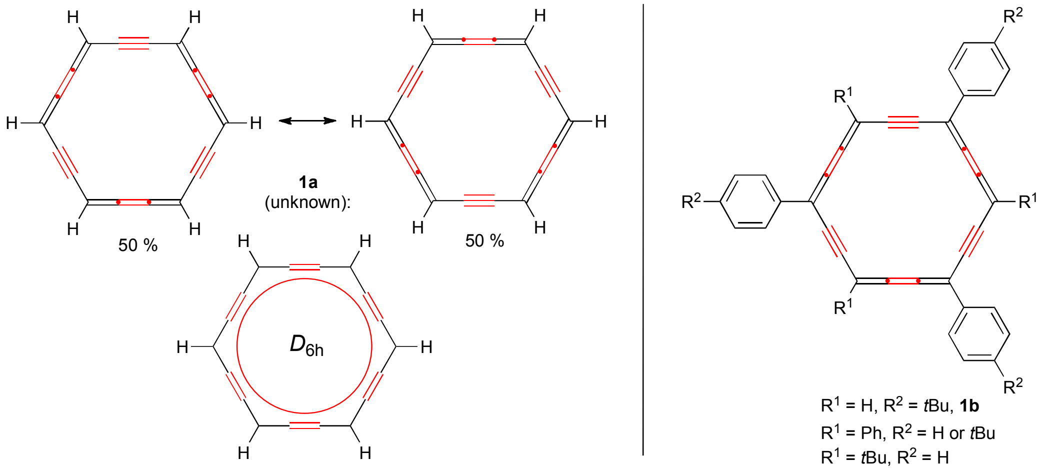
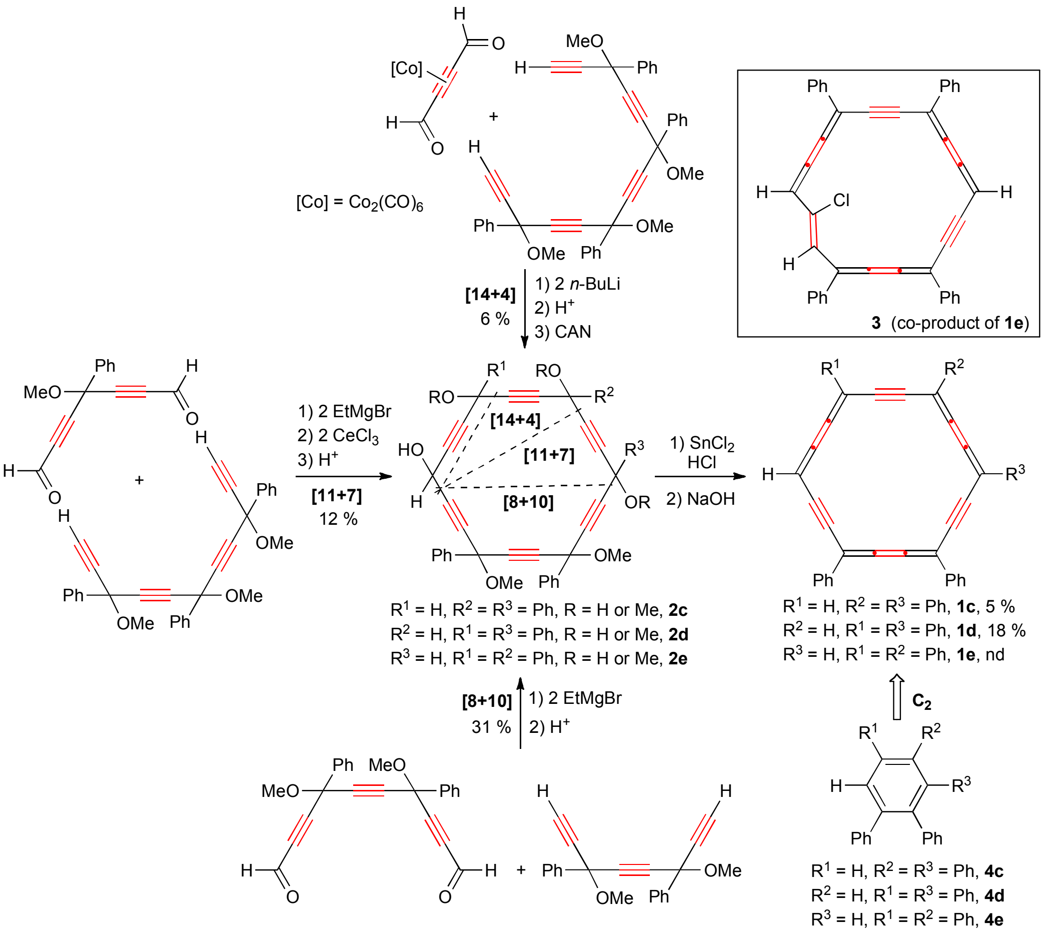


Fig. 2. The unknown unsubstituted *carbo*-benzene **1a** and substituted octupolar representatives among which the triaryl representative **1b**.

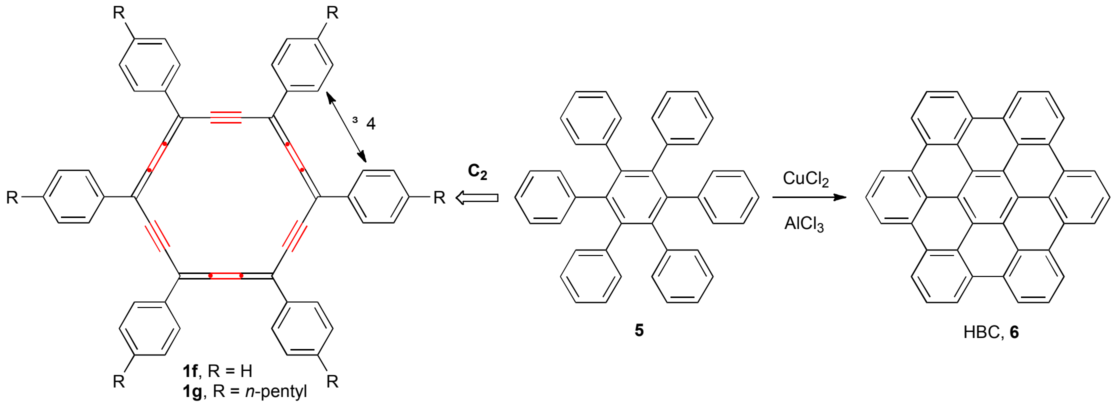
While the [6]pericyclynediol precursors **2c** and **2d** of the dipolar tetraphenyl-*carbo*-benzenes **1c** and **1d** were prepared in low yields through [14+4] and [11+7] cyclization routes,[41b,44d] the precursor **2e** of the quadrupolar *carbo*-benzene **1e** was obtained in a higher 31 % yield through a [8+10] route (Scheme 1).[44e] The corresponding processes of addition of diacetylenic dinucleophiles onto dialdehydic dielectrophiles were performed through the use of organo-lithium, -cerium or -bromomagnesium reagents respectively. The *carbo*-benzenes **1c** and **1d** were then isolated as pure samples after reductive aromatization by treatment with $SnCl_2$/HCl,[42,45] while **1e** was obtained in mixture with a side-product **3** resulting from the addition of HCl to a triple bond of one of the edges of the macrocycle.[43] In the absence of HCl, the formation of **3** can be prevented, but the reaction is then slower, leading to partial polymerization. The three regioisomers **1c-e** of tetraphenyl-*carbo*-benzene are stable and exhibit similar physico-chemical characteristics, such as comparable UV-vis absorption spectra (λ_{max} = 441 ± 3 nm) and similar ^{1}H NMR deshielded signals of the *ortho* protons of the phenyl substituents due to the aromaticity-driven strong diatropic ring current of the C_{18} macrocycle (δ_{1H} = 9.53 ± 0.03 ppm). The parent non-expanded tetraphenylbenzene molecules **4c-e** are known,[46] **4c** exhibiting aggregation-enhanced photoluminescence properties,[46a] while neither its *carbo*-mer **1c** nor the regioisomers **1d** and **1e** are luminescent, as most of the *carbo*-benzenes.



Scheme 1. Synthesis of the three regioisomers **1c**, **1d** and **1e** of tetraphenyl-*carbo*-benzene.

2.2. Hexa-homo-substituted *carbo*-benzenes

Besides the above illustrations **1b-e**, most of the known *carbo*-benzenes are fully (hexa-) substituted. Few of them can be regarded as ”homoleptic” by reference to a coordination chemistry term, where the C_{18} core plays the role of a hexa-coordinated center: the hexaphenyl representative **1f** has thus been prepared first through a 16-step [11+7] route by Ueda *et al.*,[41b] and later on through an alternative nine-step [14+4] route.[42,44d,45] The parent hexaphenylbenzene **5** was notably used as precursor for the synthesis of hexabenzocoronene (HBC) **6** by a Scholl-type reaction (Scheme 2).[47] Among other applications, this nanometric graphene fragment was, for example, recently described to be an efficient carbon source for the fabrication of photoluminescent quantum dots.[48] In the *carbo*-mer series, the approach cannot be applied for the preparation of the challenging *carbo*-HBC or related targets (Scheme 2), but recent progresses in the study of such bidimensional *carbo*-graphene fragments are discussed in section 3.

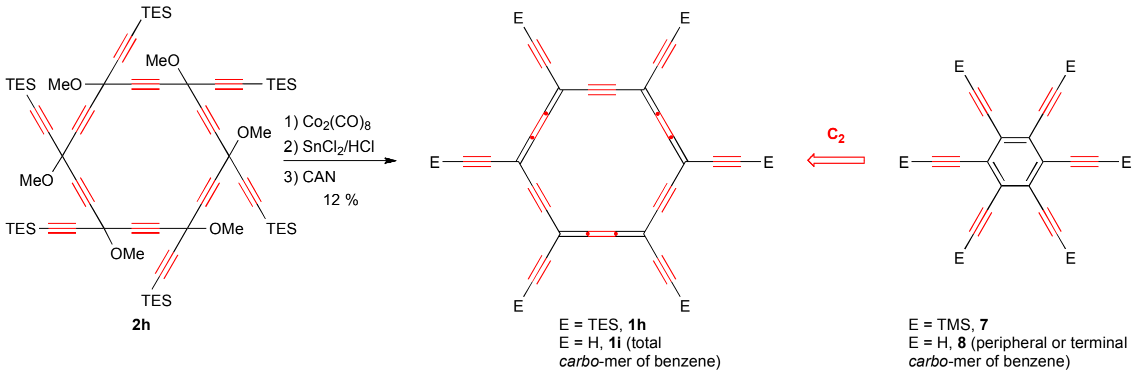


Scheme 2. The hexaphenyl- and hexa-*para*-*n*-pentylphenyl-*carbo*-benzenes, and a parent hexaphenylbenzene allowing Scholl-type oxidation, forbidden in the *carbo*-meric series.

Very recently, the more soluble hexa-*n*-pentyl-substituted analog **1g** of **1f** was also prepared through a [8+10] cyclization strategy, involving a C_8 triyne as dinucleophile and a C_{10} diketone (instead of a dialdehyde, see Scheme 1) as dielectrophile.[49]

In 2007, hexa(triethylsilylethynyl)-*carbo*-benzene **1h** was reported as a protected version of the total *carbo*-mer of benzene where C_2 units are inserted into all the C⎓C and C–H bonds of benzene.[42,50] The preparation of this unique example of non-arylated homoleptic *carbo*-benzene required a modified aromatization procedure from the hexaoxy-hexaalkynyl-[6]pericyclyne **2h** involving a transient coordination of (undefined) triple bonds with $Co_2(CO)_6$ before treatment with $SnCl_2$/HCl, this reductive system being unproductive from crude **2h** (Scheme 3). The absence of aryl substituents at the vertices of **2h** is indeed prone to induce a relative destabilization of the trialkynylcarbenium intermediate generated upon direct acidic treatment: the stabilization is however restored in Nicholas-type [6]pericyclynyl-

$Co_2(CO)_6$ complexes which then readily undergo sequential reduction, leading to **1h** after oxidative removal of the $Co_2(CO)_6$ auxiliaries. Treatment of **1h** with TBAF did not allow isolation of the deprotected total *carbo*-mer of benzene **1i**, possibly because of the insolubility of this $C_{30}H_6$ target. *Ab initio* and DFT calculations showed that the *carbo*-aromatic character of **1i** is similar to that of any *carbo*-benzene, albeit slightly lower regarding the magnetic criterion (NICS values at the center of the rings: -17.8 ppm for **1i** *vs* -19.8 ppm for the unsubstituted *carbo*-benzene $C_{18}H_6$ **1a**).[51] **1i** is also the ring *carbo*-mer of hexaethynylbenzene **8**, the synthesis of which was first reported by Vollhardt *et al.* from the hexasilylated precursor **7**,[52] and which was later used for the preparation of propeller-shaped dehydrobenzo[14]annulenes.[53]

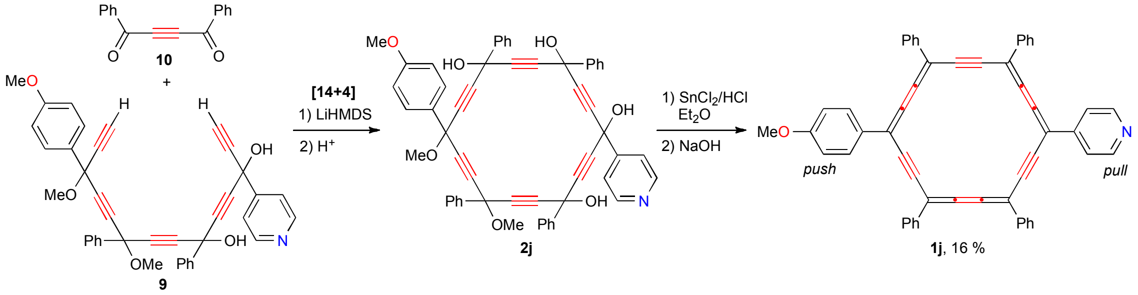


Scheme 3. Hexaalkynyl-*carbo*-benzenes, total *carbo*-mer of benzene, and parent hexaalkynylbenzenes. TES = $SiEt_3$.

2.3. Hexa-hetero-substituted *carbo*-benzenes

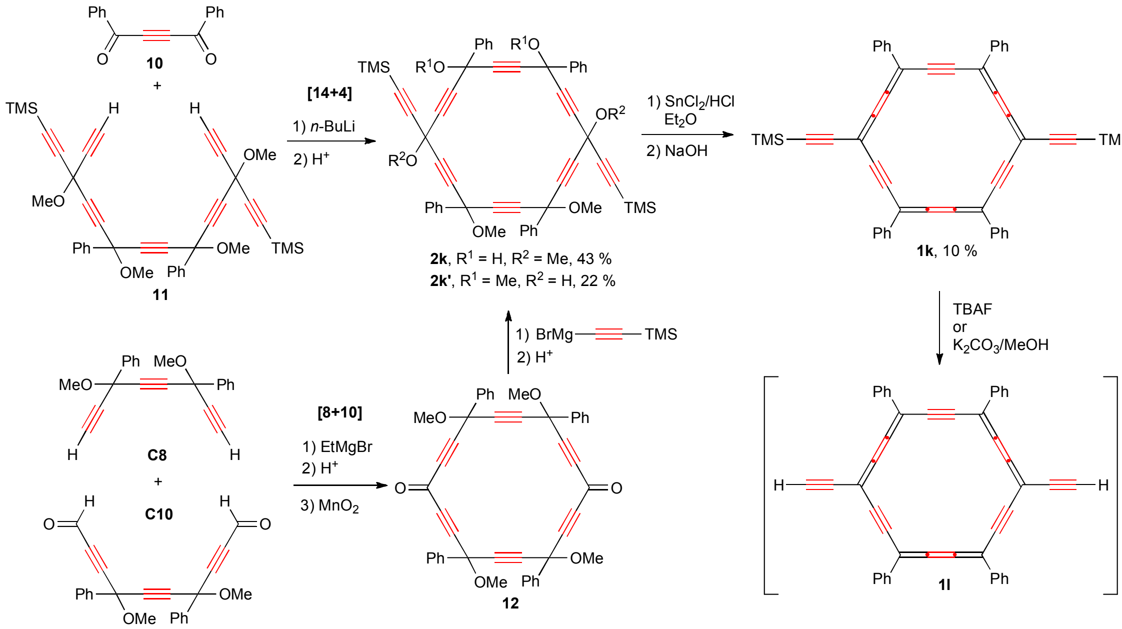
Besides the few homoleptic *carbo*-benzenes **1f-h**, most of the other representatives bear two kinds of substituents at least, one of them corresponding to phenyl groups. Most of the known *carbo*-benzenes are indeed tetraphenylated with more or less functional substituents at the opposite 1,10-vertices, namely in *para*-positions of the C_{18} macrocycle. Beside a single example of dipolar *p*-hetero-disubstituted *carbo*-benzene **1j**,[45] many quadrupolar *p*-homo-disubstituted-*carbo*-benzenes have been reported.

The dipolar push-pull pyridyl-anisyl-*carbo*-benzene **1j** was targeted for its second-order nonlinear optical (NLO) properties, which were beforehand theoretically calculated.[54] The totally dissymmetric [6]pericyclynetetraol precursor **2j** was synthesized through a [14+4] cyclization step between the pentayne **9** and dibenzoylacetylene **10** (Scheme 4),[44d] then converted to the poorly soluble dipolar *carbo*-benzene **1j** in 16 % yield upon treatment with $SnCl_2$/HCl. NLO properties of **1j** were experimentally studied by electric-field-induced second-harmonic (EFISH) measurements of the quadratic hyperpolarizability, which was estimated to be *ca* $\beta \approx 66\ 10^{-30}$ cm^5 esu^{-1},[55] in accordance with ZINDO calculations.[54]



Scheme 4. The [14+4] synthetic approach to the push-pull dipolar *carbo*-benzene **1j**.

Among numerous quadrupolar *p*-homo-disubstituted-*carbo*-benzenes, the *p*-dialkynyl-*carbo*-benzene **1k** is the sole representative that was prepared through a [14+4] approach where the exocyclic trimethylsilylethynyl substituents are anchored in an early stage of the synthesis, *i. e.* on the C14 precursor **11** (Scheme 5).[44d] The [14+4] macrocyclization step proved quite efficient, giving **2k** in a 43 % yield.[45] Other quadrupolar *carbo*-benzenes were obtained through the optimal, lately divergent [8+10] cyclization route from the **C8** diyne and the **C10** dialdehyde, leading, after an additional oxidation step, to the key [6]pericyclynedione **12**. The centro-symmetric *carbo*-benzene targets are readily accessible from the diketone **12** in two steps (Scheme 5):[44e] a double addition of organo-lithium or -bromomagnesium nucleophiles followed by reductive aromatization of the resulting [6]pericyclynediol.

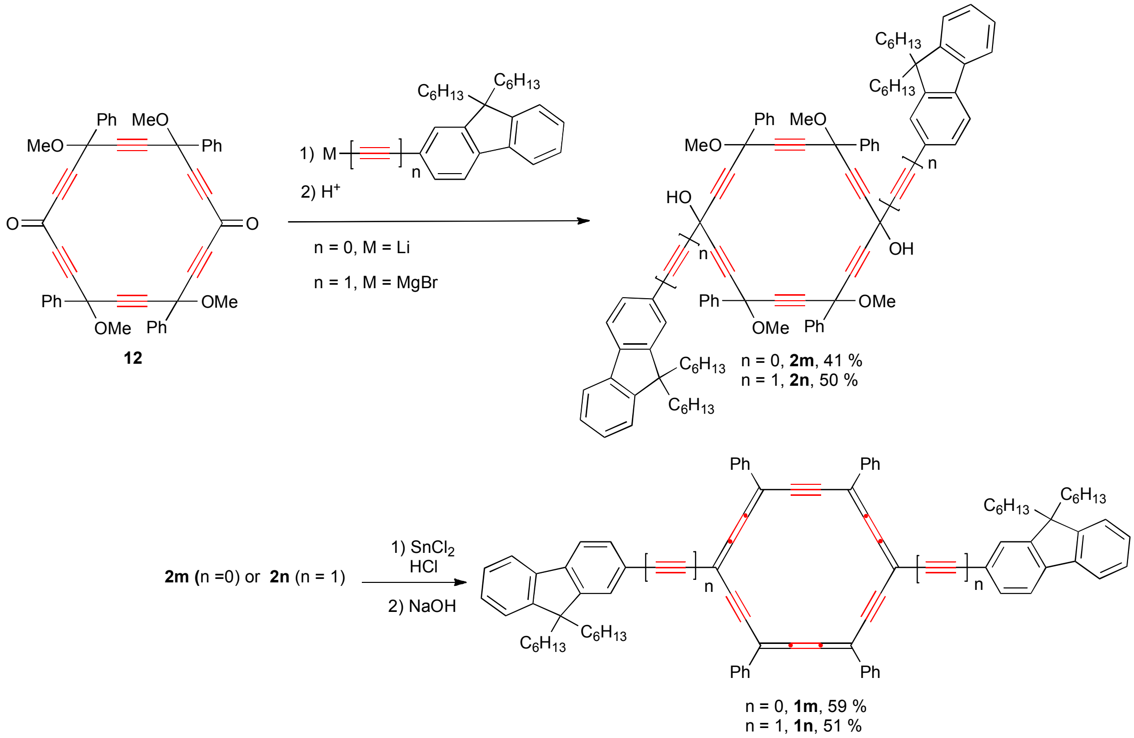


Scheme 5. The [8+10] and [14+4] routes to the *p*-dialkynyl-*carbo*-benzene **1k**.

The efficiency of this two-step strategy from the [6]pericyclynedione **12** was first examined for the preparation of the [6]pericyclynediol **2k'**,[44e] an analogue of **2k** previously obtained using the [14+4] approach, before being applied to the preparation of two categories of quadrupolar *carbo*-benzenes: (i) the all-hydrocarbon representatives or C-silylated version thereof like **1k**, and (ii) oxygen- or nitrogen-functional derivatives.

2.3.1. All-hydrocarbon p-disubstituted carbo-benzenes

All attempts at desilylation of **1k** failed to afford the purely hydrocarbon *p*-diethynyl-*carbo*-benzene **1l** (Scheme 5), the insolubility of the obtained black material preventing unambiguous spectroscopical characterization.[56] In the pure hydrocarbon series, two *carbo*-benzenes bearing fluorenyl fluorophores have been recently prepared through the above-described two-step strategy from **12** (Scheme 6). To enhance solubility, two *n*-hexyl chains were introduced at the C-9 position of the selected 2-bromofluorene precursor. The fluorene motifs were anchored to the C_{18} macrocycle of **12** either directly in **2m** after lithium-bromine exchange, or through an ethynylene arm in **2n** after Sonogashira coupling with trimethylsilylacetylene, protodesilylation, and deprotonation with EtMgBr.[57] The [6]pericyclynediols **2m** and **2n** were then reduced to the corresponding *p*-bis-fluorenyl-*carbo*-benzenes **1m** and **1n** by $SnCl_2$/HCl treatment (Scheme 6). The increase of the π-delocalization extent in **1n** with respect to **1m** has a negligible effect of the absorption properties, these two chromophores exhibiting quasi-superimposable UV-vis spectra and comparable λ_{max} values (492 nm for **1m** and 494 nm for **1n**). These spectroscopic data were accurately reproduced by TD-DFT calculations, and were interpreted through a four-orbital transition pattern similar to the Gouterman model for porphyrins.



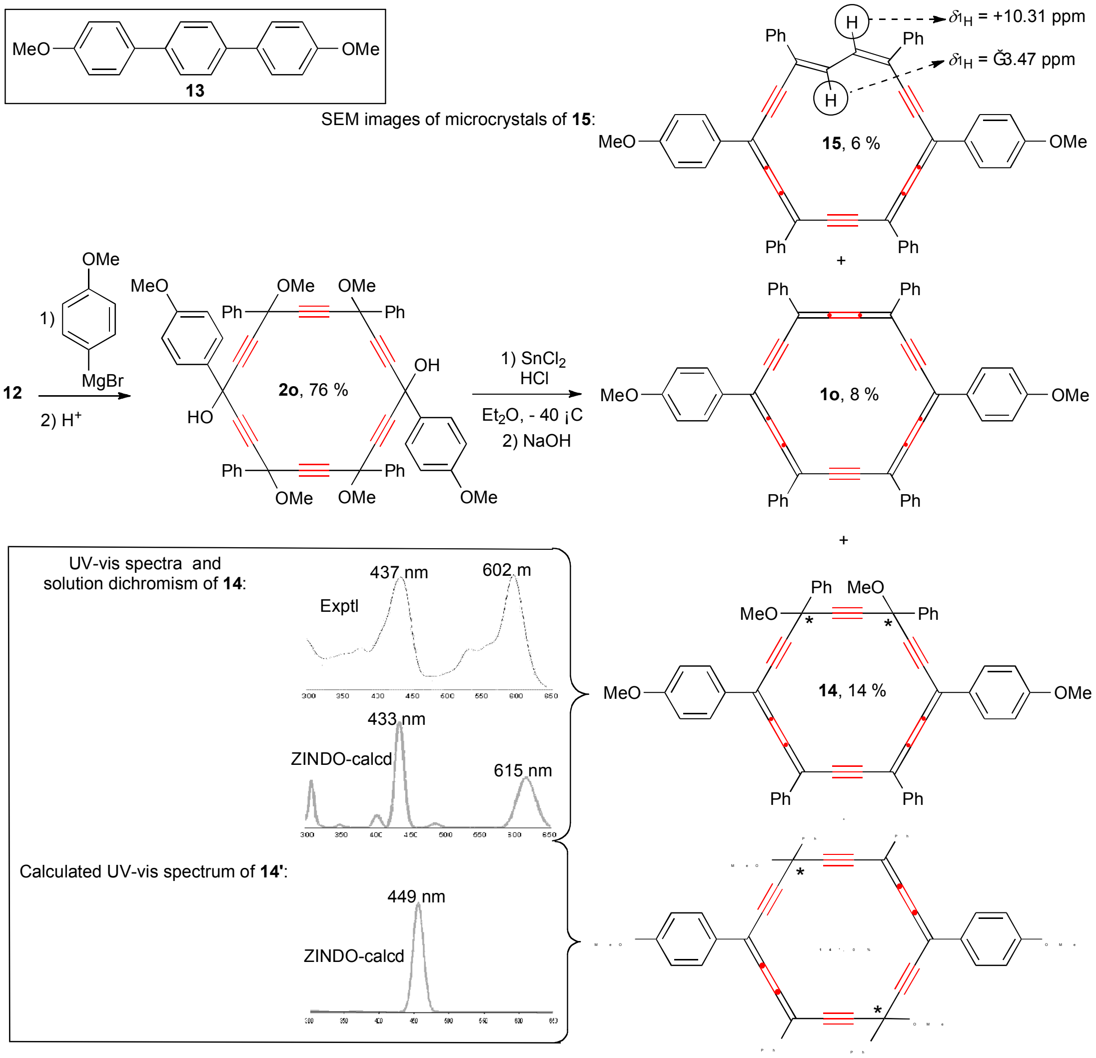
Scheme 6. Two-step synthesis of *p*-bis-fluorenyl-*carbo*-benzenes **1m** and **1n** from the [6]pericyclynedione **12**.

The fluorophore-substituted *carbo*-benzenes **1m** and **1n** were found to be weakly emissive at *ca* 650 nm, while their precursors **2m** and **2n** displayed intense emission bands at *ca* 320 nm corresponding to the intrinsic fluorescence of the fluorene moieties. Quadrupolar molecules with two donor substituents on a π-conjugated backbone are presented as plausible candidates for two-photon absorption (2PA).[58] The 2PA cross section (σ_{2PA}) of **1m** and **1n** was thus examined by the Z-scan technique, which is commonly used for the study of third order NLO properties of non-fluorescent molecules.[59] Measurements performed with femtosecond laser pulses at 800 nm indicated that the 2PA efficiency of **1n** (σ_{2PA} = 656 GM) is *ca* twice higher than that of **1m** (σ_{2PA} = 336 GM).[57] Despite the constancy of the λ_{max} value (see above), this trend for σ_{2PA} was *a priori* foreseeable from the increase of the conjugation extent in **1n** *vs* **1m**. The full 2PA spectrum of **1n**, interpolated from σ_{2PA} values at discrete wavelengths ranging from 650 to 900 nm, shows a maximum 2PA efficiency (of *ca* 800 GM) at 750 nm. This is in agreement with the TD-DFT-calculated maximum 2PA wavelength at 708 nm, which corresponds to the $4A_g$ excited state of **1n** (albeit with a lower calculated absolute cross-section value of 349 GM). Within the sum-over-states (SOS) scheme, the main contribution of intermediate 1PA excited states arises from a $2A_u$ state, which is indeed very close to half the energy of the $4A_g$ state.

A recent synthesis of other fluorenyl-substituted *carbo*-benzenes by a totally different approach is reported in section 2.4.

2.3.2. Oxygen- or nitrogen-functional p-disubstituted carbo-benzenes

Replacement of the fluorenyl donors of **1m** and **1n** (see section *2.3.1*) by anisyl donors defines an alternative quadrupolar *carbo*-benzenic candidate for 2PA. This *p*-dianisyl-*carbo*-benzene **1o**, a tetraphenylated derivative of the central ring *carbo*-mer of the terphenyl fluorophore **13** (Scheme 7),[60] was obtained by the two-step procedure from the key [6]pericyclynedione **12**.[61] In this particular case, classical reductive treatment of the diol intermediate **2o** (prepared in 76 % yield from **12**) with $SnCl_2$/HCl led to two *carbo*-chromophores of unprecedented types, **14** and **15**, along with the *carbo*-benzene target **1o** which was isolated in 8 % yield (Scheme 7). Nevertheless, the very weak fluorescence and very poor solubility of **1o** prevented any measurement of the 2PA cross-section.



Scheme 7. Synthesis of the *p*-dianisyl-*carbo*-benzene **1o** and properties of its sub- and over-reduced side-products **14** and **15**, respectively.

The side-products **14** and **15** correspond to sub-reduced and over-reduced compounds, respectively. The sub-reduced chromophore **14** was isolated in 14 % yield, as a mixture of two *cis*/*trans* diastereoisomers that could be resolved by semi-preparative HPLC.[61] This first example of *carbo*-cyclohexadiene, possesses only two butatriene units (instead of three in *carbo*-benzenes) which could be either conjugated or not. As the corresponding regioisomers **14** and **14'** could not be *a priori* distinguished by NMR, IR nor UV-vis spectroscopy, in the absence of crystallographic data, the structure of the isolated product was ascertained by comparison of the experimental UV-vis absorption spectrum with theoretical spectra of both the isomers **14** and **14'** calculated at the ZINDO or TD-DFT level (Scheme 7).[61] The two-band UV-vis spectrum of the isolated *carbo*-cyclohexadiene was found to correspond to that calculated for the conjugated structure **14**, the spectrum of the non-conjugated isomer **14'** being predicted to exhibit as single band, as very recently confirmed after isolation of the first *carbo*-cyclohexa-1,4-diene (see section 2.5, Scheme 11). The two-intense-band spectral profile of **14** is actuallycorrelated with the uncommon dichromic behaviour of solutions of **14**, appearing either blue or purple depending on the length of the optical path crossing the solution (Scheme 7).[62] In spite of a non-aromatic C_{18} macrocycle, the *carbo*-cyclohexadiene **14** was found to be relatively stable.

The over-reduced chromophore **15** is a dihydro-*carbo*-benzene resulting from a formal regioselective and *trans*-stereoselective reduction of one triple bond of **1o**. The magnetic macrocyclic aromaticity of **15** is dramatically evidenced by a strong relative ^{1}H NMR shielding of the protons of the *trans* sp^2C*H*–sp^2C*H* bond, at +10.31 ppm and –3.47 ppm for the exocyclic and endocyclic nuclei respectively. These experimental data are consistent with the DFT-calculated NICS(0) value at the centroid of **15** (-12.8 ppm) which is comparable to that of the *carbo*-benzene **1o** (-13.5 ppm). Noteworthy, the dihydro-*carbo*-benzene **15** spontaneously gives tubular micro-crystals of hexagonal section upon solvent evaporation from almost any organic solutions (see SEM image in Scheme 7).[61]

While the sub-reduced *carbo*-cyclohexadiene **14** was shown to be an intermediate on the way to the *carbo*-benzene **1o**, the over-reduced product **15** could not be generated from **1o** under these experimental conditions, the reduction of the triple bond thus occurring at an earlier stage.

Nitrogen-functional quadrupolar *carbo*-benzenes, analogues of the dianisyl chromophore **1o**, were also envisaged from a more fundamental viewpoint. The issue was to study the formal "π-frustration" induced by two strong π-donating substituents facing each other through the highly π-electron rich *carbo*-benzene core. The π-frustration effect was considered in two series of *carbo*-benzene derivatives, where two nitrogen atoms are conjugated to the C_{18} macrocycle through either a *p*-phenylene linker or an ethenyl(ethynyl)ene linker (Fig. 3).[63]

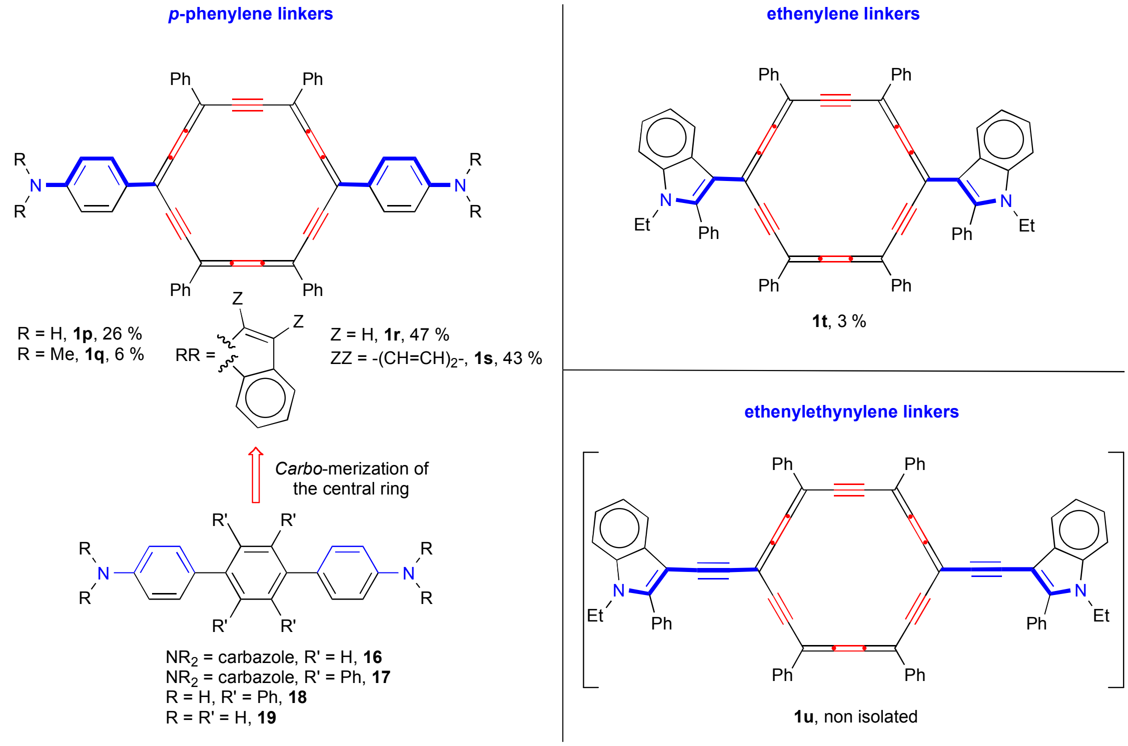
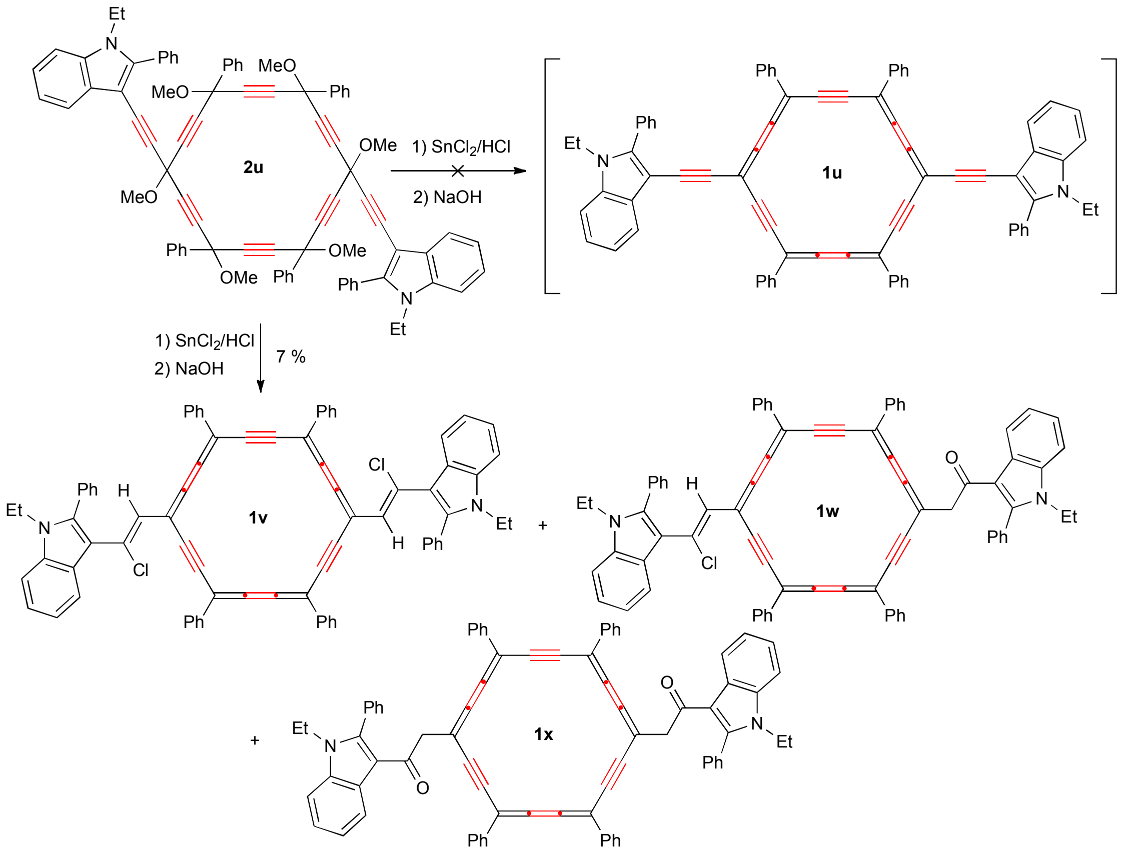


Fig. 3. The two series of π-frustrated *carbo*-benzenes. Percentages correspond to yield of the two-step syntheses from the [6]pericyclynedione **12** (see Scheme 5).

The amino-π-frustrated *carbo*-benzenes **1p-u** were prepared in 3 to 47 % yields in two steps from the [6]pericyclynedione **12**. The representatives **1p-s**, containing *p*-phenylene linkers, were found stable. In contrast **1t** and **1u**, containing ethenyl(ethynyl)ene linkers, were found respectively poorly stable and not stable enough to be isolated, and this in spite of the stabilization of the “enamine” motifs by benzannelation in an indole core. The π-frustration is thus more significant when the nitrogen atoms are conjugated to the macrocycle across an ethenyl(ethynyl)ene linker than across a *p*-phenylene linker, the latter playing the role of an aromatic insulator between the C_{18} core and the nitrogen donor.

When the nitrogen atoms are conjugated to the macrocycle through a five-bond linker comprising an acetylenic spacer (Fig. 3, *bottom right*), the *carbo*-benzene target **1u** could not be isolated. The reductive aromatization of the [6]pericyclynediol **2u** with $SnCl_2$/HCl is indeed accompanied here by a regio- and stereo-selective addition of HCl to the exocyclic triple bonds, thus giving the *carbo*-benzene **1v** (Scheme 8).[63b] The π-frustration between the indolyl donors and the electron-rich *carbo*-benzene core thus enhances the nucleophilicity of the acetylenic spacers, making them extremely sensitive to the acidic conditions used. The chloroethenylene linkers of the still π-frustrated *carbo*-benzene **1v** were found to react with traces of water upon purification on silicagel, giving two other *carbo*-benzenes **1w** and **1x**, themselves not very stable.



Scheme 8. Illustration of the π-frustration effect on the reactivity of ethynylene and ethenylene spacers between indolic donors and a *carbo*-benzene core.

Amino-π-frustration effects were also appraised by UV-vis spectroscopy. Comparison of the maximum absorption wavelength of the *carbo*-chromophores **1p-s** indeed showed that the relative aromatic character of the π-conjugating linkers between the nitrogen donor and the C_{18} core has more effect than their relative length, the bathochromic shift induced by donor substituents being larger with the ethenylene linkers of **1t** than with the more π-extended *p*-phenylene linkers of **1p-s**.[63b]

The emission properties of the stable fluorophore-substituted *carbo*-benzenes **1r**, **1s** and **1t**, substituted by 4-(indolyl)phenyl, 4-(carbazolyl)phenyl and indol-3-yl motifs, respectively (Fig. 3), were also studied. As mentioned above for the fluorene-substituted *carbo*-benzenes **1m** and **1n** (Scheme 6), **1r** and **1s** are almost not fluorescent, at least in the analyzed visible region. The fluorescence quenching can tentatively be explained by the high absorbance of the *carbo*-benzene core, thus instantly absorbing the emitted photons. In the case of **1t,** however, a significant emission occurs at 303 and 603 nm upon excitation at 242 and 503 nm, respectively.[63b,64] This unique behaviour of **1t** can be correlated with its particularly low extinction coefficient (ε = 41000 L.mol^{-1}.cm^{-1}) as compared to those of **1m**, **1n**, **1r** and **1s** (ε > 330000 L.mol^{-1}.cm^{-1}). Within the original spirit of the definition of *carbo*-mers, it is noteworthy that parent molecules of some of the *carbo*-benzenes described above are known. For instance, the non-substituted and tetraphenyl derivatives of the bis-carbazolyl-triphenylene parents (**16** and **17**) of **1s** were considered for their optoelectronic properties, and particularly for the design of phosphorescent organic light emitting diodes (PHOLEDs) (Fig. 3).[65] The *p*-dianilinyl-*carbo*-benzene **1p**, initially described for the fundamental study of π-frustration, was more recently examined for its charge transport properties at the single molecule level. The highly π-unsaturated and symmetric structure of *carbo*-benzenes is indeed *a priori* attractive for the elaboration of molecular junctions. Related oligoethynylenes, oligophenylenes, oligophenylethynylenes (OPEs) or porphyrins, bearing functional termini playing the role of anchors to nanoelectrodes, have indeed been shown to exhibit charge transport properties.[66] The single molecule conductance (SMC) of **1p** was thus studied by the scanning tunneling microscopy (STM) break-junction technique (STM-BJ) developed by N. J. Tao *et al.* in 2003,[67] and based on a statistical analysis of thousands of current/distance traces recorded upon approaching and retracting a STM gold-tip from a gold-substrate covered by a layer of *a priori* conducting molecules. Among the many possible anchoring functional groups proposed in the literature, the NH_2 groups has appeared as one of the most efficient.[66c,68] The *carbo*-benzene **1p**, containing two such groups, were thus shown to exhibit a conductance of 106 nS (Fig. 4), a remarkable value for a molecule of this size (1.94 nm N···N distance measured by X-ray crystallography).[63a,69] This value is indeed *ca* 10 times higher than those measured for molecules of similar or shorter length bearing the same NH_2 anchoring groups,[70] such as porphyrins,[71] OPEs[66a] or hexabenzocoronenes.[72] The *carbo*-benzene **1p** was also shown to be about 40 times more conductive than a flexible linear *carbo*-*n*-butadiene reference (see section *2.6.2*, Scheme 14), a difference ascribed to the aromatic rigidity of **1p** by means of DFT-NEGF calculations.[69] Furthermore, molecular junctions of **1p** were shown to exhibit a field effect transistor behavior under electrochemical gating conditions.

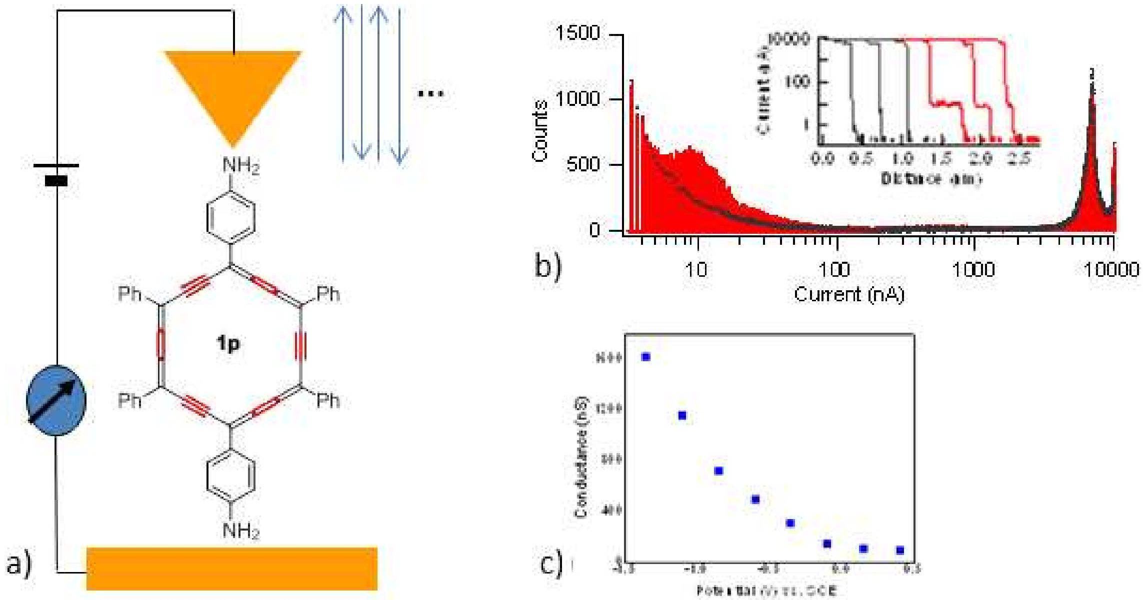


Fig. 4. a) Principle of the STM-BJ method used for measuring the SMC of the *carbo*-benzene **1p**; b) full histogramm constructed from several thousands of STM-BJ experiments. The inset shows individual traces obtained with**1p** (red) and control experiments without molecular conductor (black); c) conductance *vs* gating potential for **1p**.

Parent molecules of the *carbo*-benzene **1p**, in which the central phenylene ring is not C_2-expanded, were previously reported in both the tetraphenylated form **18** and non-substituted form **19** (Fig. 3), which were used in co-polymerization processes leading to polyamides[73] or polyimides[74] exhibiting liquid crystal behaviours. The triphenylene diamine **19** has also been studied for its charge transport properties.[75] In comparison with its central ring *carbo*-mer **1p**,[69] the SMC value of **19** measured by the same STM-BJ method was found *ca* one order of magnitude smaller (14 nS for **19** *vs* 106 nS for **1p**). The triphenylenediamine **19** was also considered in several studies of the influence of the molecular rigidity[75a] or length[75c,d] on SMC.

2.4. Proaromatic *carbo*-quinoids

The concept of proaromaticity, proposed for push-pull quinoidic chromophores where the zwitterionic aromatic form is an important contribution of the ground state, was first illustrated for 6-membered rings **20**,[76] and later for 14-membered acetylenic rings **21** (Fig. 5).[77] Passing from excitation to ionization, "redox-proaromaticity" was recently proposed as a generalization applying to non-dipolar molecules. Beyond the quinone/hydroquinone system, it was thus illustrated for difluorenylidene-*carbo*-quinoid hydrocarbons **22**.[78] The non-expanded parent quinoid **23** could not be isolated because of the strong aromaticity of the corresponding C_6 benzene ring,[79] but the partly expanded C_{14} representative **24** was described in a benzannelated form preventing aromatization (Fig. 5).[80] The synthesis of the fully expanded C_{18} macrocyclic bis-fluorenylidene-*carbo*-quinoid **22** was performed from the [6]pericyclynedione **12**.

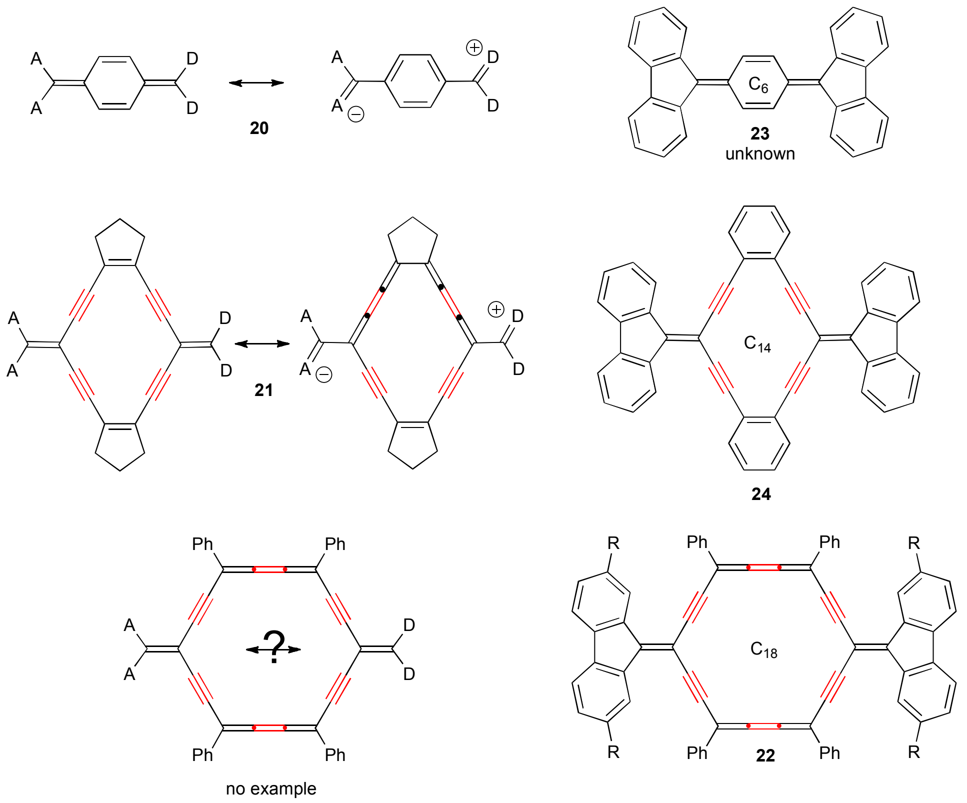
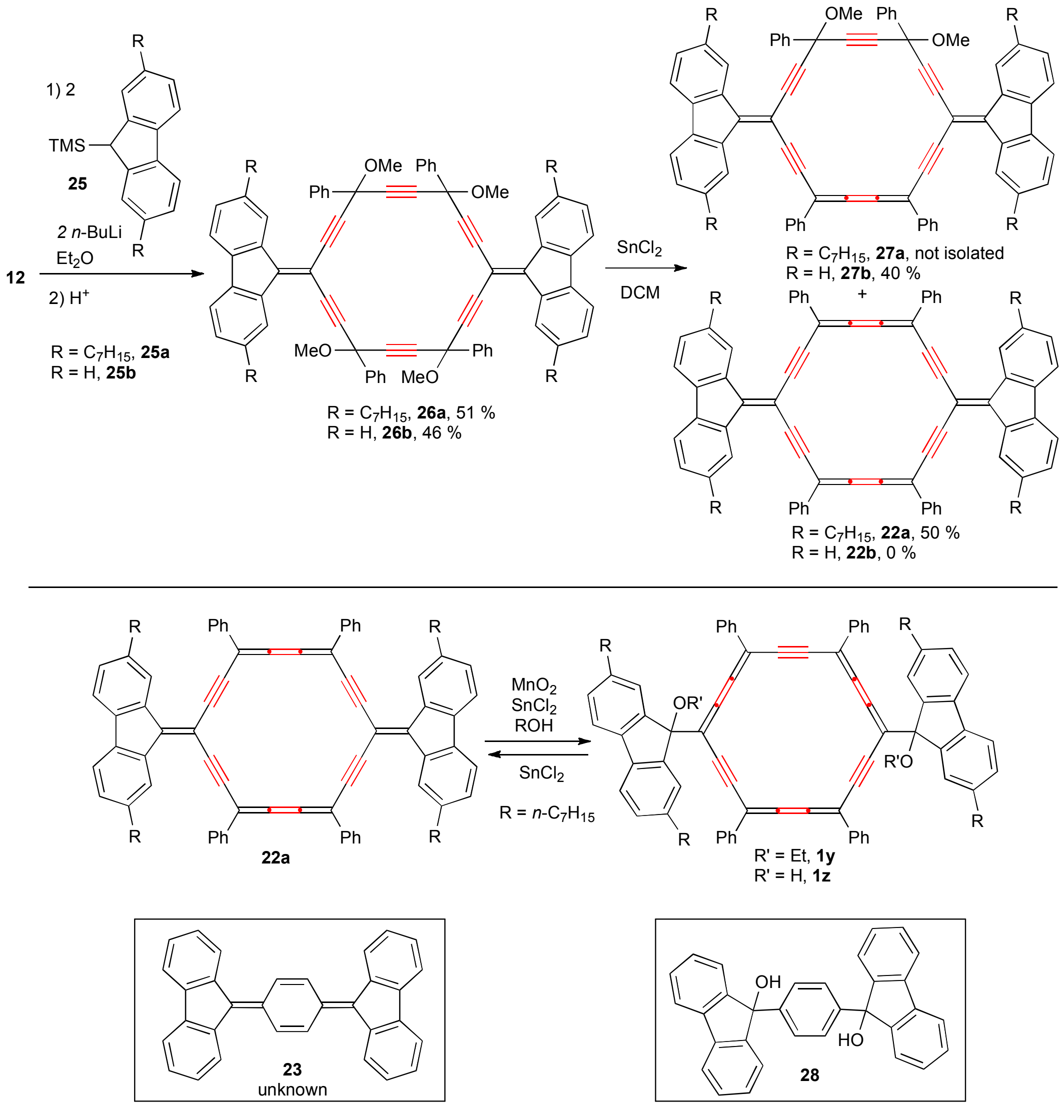


Fig. 5. Radiannulenic and dehydroradiannulenic quinoids with six-, fourteen- or eighteen-membered ring.

Peterson reaction of **25a** and **25b** with the [6]pericyclynedione **12** in diethylether gave the bis-fluorenylidene[6]pericyclynes **26a** and **26b**, respectively (Scheme 9). Treatment of **26a** with $SnCl_2$ afforded the *carbo*-quinoid **22a** in 50 % yield as a stable and soluble blue chromophore (in the same conditions, **26b** led to the partly reduced product **27b**, the insolubity of **22b** preventing proper isolation). The redox-proaromaticity of the *carbo*-quinoid **22a** was then investigated under oxidative conditions. Treatment of **22a** with MnO_2 in the presence of $SnCl_2$ and R'OH (R' = H, Et) thus led to the *carbo*-benzenes **1y** and **1z** , which were found to be less stable than **22a** in the dry state, but to exhibit the classical *carbo*-aromaticity features. The reversibility of the redox transformation was finally evidenced by $SnCl_2$-mediated reduction of **1y** to **22a**.[78] The **22a** □ **1y** interconversion thus illustrates the redox-proaromaticity of C_{18} *carbo*-quinoids.



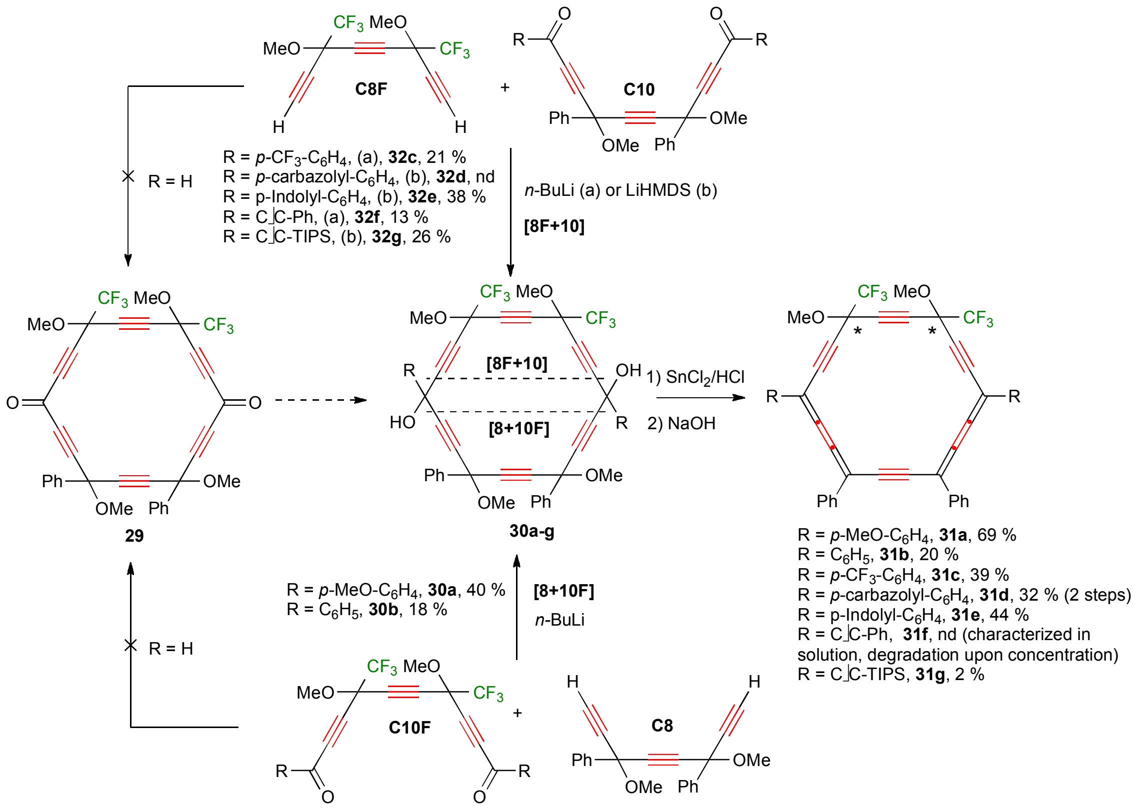
Scheme 9. Synthesis of the *carbo*-quinoid **22a** and reversible interconversion with the corresponding *carbo*-benzenes **1y** and **1z**.

The non-expanded parent molecule of the *carbo*-quinoid **22a** (or more precisely of **22b**), **23**, is not known. Nevertheless, the C_6 aromatic counterpart of **23** (**28**), parent molecule of the C_{18} *carbo*-benzene **1z**, was described and envisaged as a putative precursor of **23**.[79a] The bis-hydroxyfluorenylbenzene **28** had also been considered as a *clathrate* compound, giving crystalline inclusion compounds with various organic guests such as alcohols or acetone.[81]

2.5. Non-aromatic cyclic references of *carbo*-benzenes

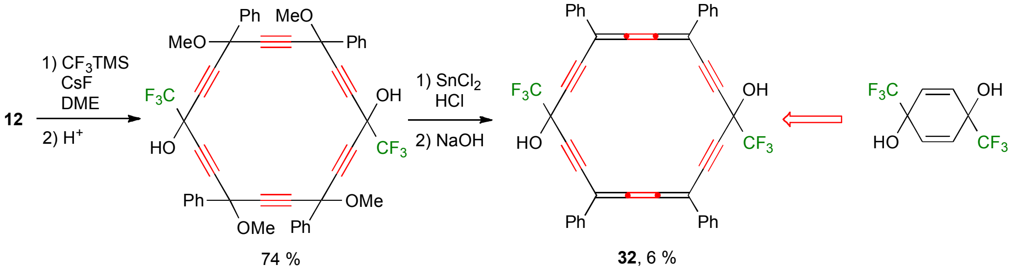
As the combination of σ-cyclic and π-acyclic characters is a key criterion in the design of accurate approximations of non-aromatic references (see Introduction), *carbo*-1,3-cyclohexadienes stand as relevant candidates for *carbo*-benzenes, just like 1,3-cyclohexadienes do for benzenic derivatives.[82]

After incidental isolation of the first example of *carbo*-1,3-cyclohexadiene **14** (Scheme 7),[61] the selective synthesis of other representatives was envisaged through a control of the sequential reduction process leading from hexaoxy[6]pericyclynes (*e. g.* **2o**) to *carbo*-benzenes (*e. g.* **1o**). The selective formation of two butatriene edges instead of three was made possible by the introduction of two CF_3 groups on adjacent vertices of the hexaoxy[6]pericyclyne precursors. The CF_3 groups were indeed expected to destabilize the carbenium centers transiently formed in the acidic medium used ($SnCl_2$/HCl), thus blocking the reduction of the bis-trifluoromethylbutyne edge. Starting from ethyltrifluoroacetate, two strategies were devised from classical [8+10] routes to *carbo*-benzenes: depending on the location of the CF_3 groups on either the C8 or the C10 synthons, [8F+10] and [8+10F] routes were thus respectively defined (Scheme 10).



Scheme 10. [8F+10] and [8+10F] cyclizations routes to the bis-trifluoromethyl-*carbo*-cyclohexadienes **31a-g**.

While the bis-trifluoromethyl-[6]pericyclynedione **29**, analogue of **12**,[44e] could not be prepared from either C10 or C10F dialdehydes (Scheme 5), application of the [8F+10] or [8+10F] strategy to diketone dielectrophiles proved efficient.[83] Two C10 diketones and five C10F ones were used, allowing the preparation the bis-trifluoromethyl-[6]pericyclynediols **30a-g** in 13-38 % yields (Scheme 10). Subsequent treatment of **30a-g** with $SnCl_2/HCl$ gave the corresponding *carbo*-1,3-cyclohexadienes **31a-g**, the dialkynyl derivatives **31f** and **31g** being much less stable than the tetraaryl ones **31a-e**. These *carbo*-cyclohexadienes were obtained as *cis*/*trans* (or *meso*/*dl*) diastereoisomeric mixtures, and most of them could be resolved by silicagel chromatography, or by crystallization for **31a**. The latter dianisyl *carbo*-cyclohexadiene was found much more stable than its tetraphenyl homologue **14** in the dry state.[61] The dichromic behaviour of **14** was also observed for solutions of **31a**, but also for solutions of other fluorinated *carbo*-cyclohexadienes, especially **31f**. These chromophores display similar UV-vis absorption spectra, with two intense absorption bands but slight differences in maximum absorption wavelengths modulating the visibility of the dichromism phenomenon. It is finally noteworthy that the dianilinyl *carbo*-1,3-cyclohexadiene **31** for R = 4-NH_2-C_6H_4 escaped to all attempts at synthesis hitherto.[83b] Besides the *carbo*-1,3-cyclohexadienes **14** and **31a-g** (Scheme 10), and beyond the theoretical study of **14'** (see section *2.3.2*, Scheme 7), one experimental example of *carbo*-1,4-cyclohexadiene **32** was recently reported.[84] The synthesis of **32** relies on the trifluoromethylation principle applied in the *carbo*-1,3-cyclohexadiene series **31a-g**. A two-step synthesis of **32** was initiated by the reaction of the [6]pericyclynedione **12** (Scheme 11) with two equivalents of the Ruppert-Prakash reagent CF_3-TMS giving, after hydrolysis of the bis-silylether intermediate, the bis-trifluoromethylated diol target in 74 % yield. After subsequent reduction with $SnCl_2$/ HCl, the *carbo*-1,4-cyclohexadiene **32** was isolated in a low 6 % yield because of a poor stability compared to the 1,3-isomer **31b**. The spectroscopic characteristics (NMR, UV-vis) of **32** are also quite different from those of **31b**. As calculated for **14'** (Scheme 7), the UV-vis spectrum of **32** exhibits a single main absorption band (at 418 nm; instead of two for **31b**) and is thus comparable to those of isolated DAB derivatives (see section 2.6).[85]



Scheme 11. Synthesis of the *carbo*-1,4-cyclohexadiene **32** from the [6]pericyclynedione **12**.

Few examples of bis-trifluoromethylcyclohexadienes, parent molecules of *carbo*-1,3- and *carbo*-1,4-cyclohexadienes **31** and **32** respectively, were reported in the literature, albeit without any aryl or alkynyl substituents on the four other vertices.[86] In a strategy related to one employed for the synthesis of **32**, treatment of *o*- and *p*-benzoquinone with the Ruppert-Prakash reagent was reported to give the corresponding bis-trifluoromethylated cyclohexadienes.[87]

2.6. Acyclic references of *carbo*-benzenes

n-Butadiene and ethylene are frequently invoked as non-aromatic components in aromatic stabilization energies (ASE) equations of benzene (see one of the simplest schemes in Fig. 6a).[88] *Carbo*-*n*-butadienes **33** and *carbo*-ethylenes **34** are thus the corresponding relevant structures for evaluation of *carbo*-benzene aromaticity, which has long been regarded as a key stabilization factor of these highly π-electron-rich molecules. Nevertheless, since σ-cyclic and π-acyclic *carbo*-cyclohexadienes **31** were also found quite stable (see section 2.5),[83] the issue remains relevant for the σ- and π-acyclic components **33** and **34**. In particular, *carbo*-*n*-butadiene (or dibutatrienylacetylene = DBA) components, **33** corresponding to the quadrupolar *carbo*-benzene series, instigated systematic studies.

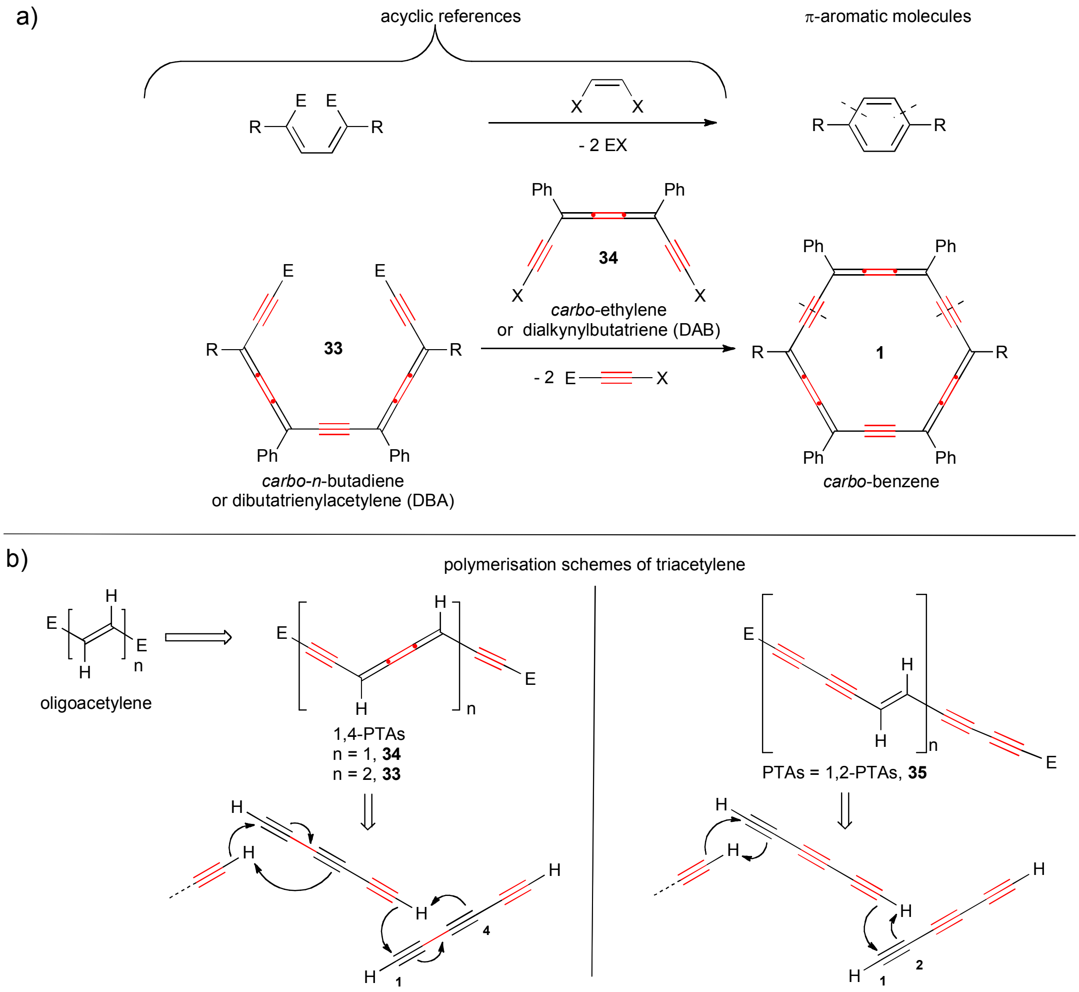
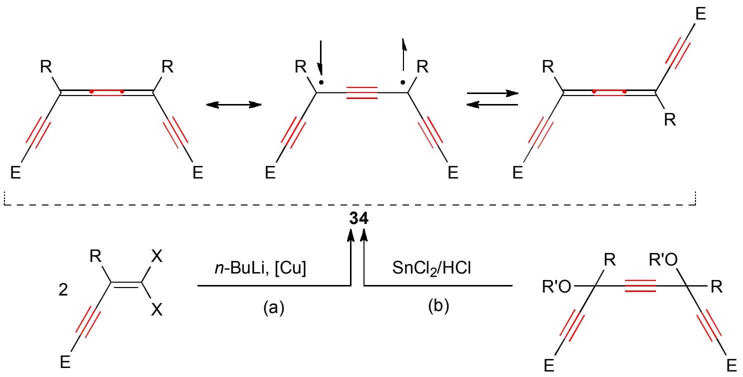


Fig. 6. a) *Carbo*-meric ASE equations for the C_{18} ring of quadrupolar *carbo*-benzenes. b) Two polymerization schemes of polytriacetylene defining the 1,2- and 1,4-isomers of polytriacetylene (PTA): the polymerization process is based on the metathesis of C–H bonds with either acetylenic HC≡C bonds (1,2) or butadiyne C≡C–C≡C units (1,4); E = end caps, *e. g.* trialkylsilyl goups.

The *carbo*-*n*-butadiene and *carbo*-ethylene structures **33** and **34** can also be presented as the first members of a regioisomeric series of the polytriacetylenes (PTAs) **35**, first exemplified in 1994,[89] and found to be stable even for high n values (Fig. 6b).[90] To distinguish between the two series, the locant 1,2- is used for the original PTAs, formally obtained by 1,2-polymerization of triacetylene (Fig 5b), while the locant 1,4- is used for *carbo*-oligoacetylenes, such as **34** for n = 1, and **33** for n = 2, formally resulting from the 1,4-polymerization of triacetylene.

2.6.1. *Dialkynylbutatrienes, substituted carbo-mers of ethylene*

The smallest DAB derivatives **34** were first exemplified by Diederich *et al.* through the di-alkynylbutatrienes **34a-34b** (with two unsubstituted vertices: R = H, Scheme 12) and tetra-alkynylbutatrienes **34c-k**.[85a-c] The stability of these DABs appeared to depend on both the substituents R and the chain caps E. They were prepared by reductive coupling of *gem*-dihaloenynes in the presence of a copper salt and *n*-BuLi (method (a) in Scheme 12). Mixtures of *cis* and *trans* isomers were obtained and a low *cis-trans* isomerization barrier was evidenced, in particular for tetraalkynyl representatives exhibiting a stabilized singlet biradical transition state.[91]

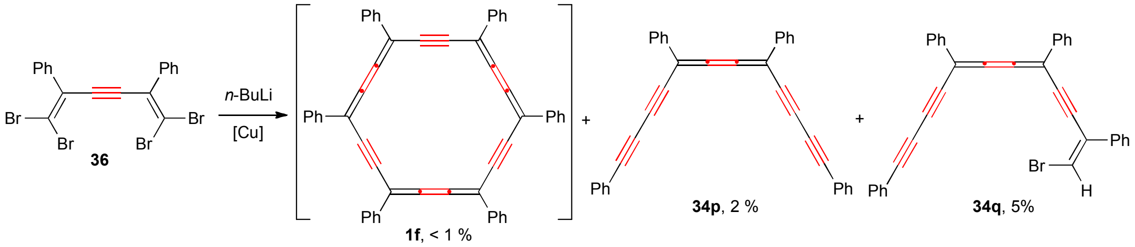


R = H, E = 4-Me$_2$N-C$_6$H$_4$X = Br ,(a), **34a**, ref 85c
R = H, E = TIPS, X = Br, (a), **34b**, ref 85c
R = ≡—TMS, E = TMS, X = Br, (a), **34c**, ref 85a
R = ≡—TIPS, E = TIPS, X = Br, (a), **34d**, ref$_{85}$a
R = ≡—TIPS, E = 3,5-(*t*Bu)$_2$C$_6$H$_3$, X = Br, (a), **34e**, ref 85c
R = ≡—TIPS, E = 4-Me$_2$N-C$_6$H$_4$, X = Br, (a), **34f**, ref 85c
R = ≡—TIPS, E = 4-MeO-C$_6$H$_4$, X = Br, (a), **34g**, ref 85c
R = ≡—TIPS, E = Ferrocenyl, X = Br, (a), **34h**, ref 85c
R = ≡—TIPS, E = 4-NO$_2$-C$_6$H$_4$, X = Br, (a), **34i**, ref 85b
R = ≡—TIPS, E = C$_6$H$_5$, X = Br, (a), **34j**, ref 85b
R = ≡—TIPS, E = *t*Bu, X = Br, (a), **34k**, ref 85b
R = CF$_3$, E = TIPS, X = Br, (a), **34l**, ref 85d
R = Ph, E = TIPS, X = Cl or Br, (a) **34m**, ref 85d
TBAF
R = Ph, E = H, **34n**, ref 85d
R = Ph, E = Me, R' = Me, (b), **34o**, ref 85d

Scheme 12. Complementary synthetic approaches to di- and tetra-alkynylbutatrienes.

Another series of DABs with non-alkynyl substituents R (= Ph, CF_3) was later described. It was accessed by two methods: by the method previously used by Diederich *et al.* (route (a), Scheme 12), and by an alternative reductive elimination procedure from dioxytriynes (route (b), Scheme 12).[85d] The first DABs with non-bulky caps, **34n** (E = H) and **34o** (E = Me), were thus obtained and found stable in solution only, polymerisation occurring upon concentration to dryness. The stable diphenyl- and bis(trifluoromethyl)- DABs **34m** and **34n** were shown to undergo rapid isomerization at room temperature, as previously reported for tetraalkynylbutatrienes.[85b,c]

The bis-*gem*-dihalodienyne **36** was also involved in a sequential reductive coupling process, leading to a complex mixture from which the dialkynylbutatrienes **34p** and **34q**, resulting from competing Fritsch-Buttenberg-Wiechell (FBW) rearrangements,[92] could be isolated (Scheme 13). A third product, namely the targeted hexaphenyl-*carbo*-benzene **1f**, could be identified by its characteristic orange spot on TLC plates and deshielded ^{1}H NMR signals (in particular a doublet at +9.50 ppm) in a mixture with unidentified products.[85d]

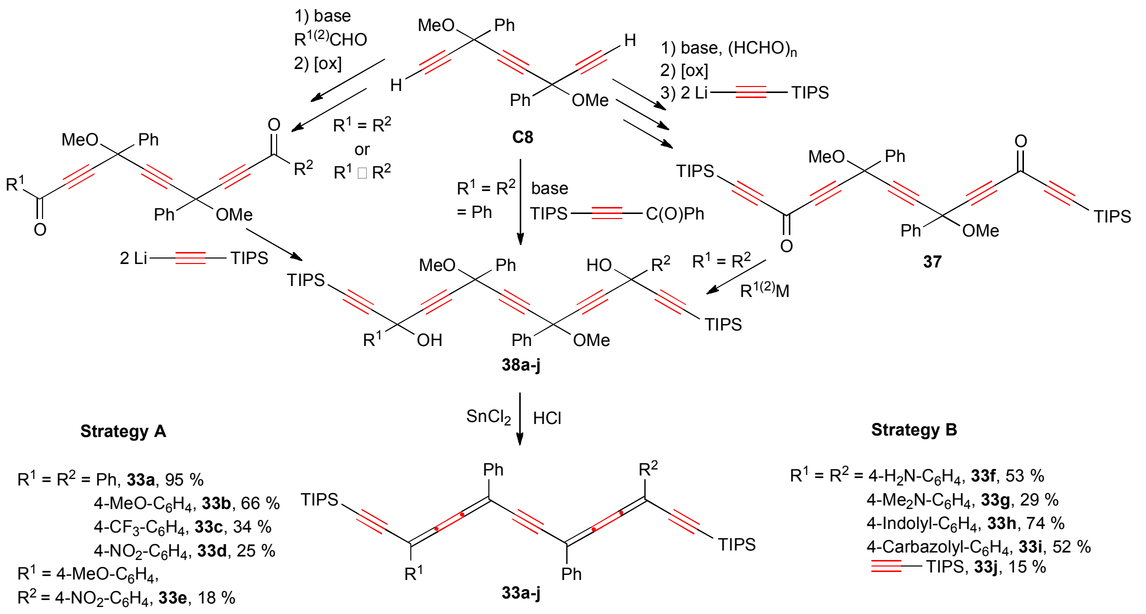


Scheme 13. Sequential dehalo-coupling of the tetrabromodienyne **36**.

2.6.2. Dibutatrienylacetylenes, substituted carbo-mers of n-butadiene

A series of *carbo*-*n*-butadienes **33** diversely substituted at the C-3 and C-12 positions was accessed through two strategies from the common triyne **C8**, also used for the preparation of the [6]pericyclynedione **12** (Scheme 5).[63a,93] The first strategy (A, Scheme 14) relies on the addition of a disalt of **C8** to aldehydes or propargylic ketones bearing the envisaged C-3- and C-12-substituents in **33**. This strategy allows the introduction of two different substituents R^1 and R^2 on the same *carbo*-*n*-butadiene motif through two successive additions of **C8** to two different electrophiles. It was first applied to the preparation of symmetrical *carbo*-*n*-butadienes **33a-d** bearing phenyl substituents at the C-6 and C-9 positions and other aryl substituents at the C-3 and C-12 positions, before being used for the synthesis of the dissymmetrical *carbo*-*n*-butadiene **33e**.[93b] The second strategy (B, Scheme 14) is based on the preparation of the pentaynedione **37**, to which the R^1 and R^2 substituents can be anchored, with $R^1 = R^2$ in this case. This lately divergent method allows addition of fragile aminophenyl substituents of the *carbo*-*n*-butadienes **33f-i** at a late stage of the synthesis.[63a] The second method was also applied to the preparation of the tetralkynyl-*carbo*-*n*-butadiene **33j** (Scheme 14). [93b]

The two strategies A and B end up with a $SnCl_2$-mediated reductive elimination step from the pentaynediols **38a-j**, affording the stable tetraarylated *carbo*-*n*-butadienes **33a-i** in 25-95 % yields, and the less stable tetraalkynylated derivative **33j** in a lower 15 % yield. ^{1}H NMR spectroscopy indicated that all the disymmetrical DBAs **33a-i** were obtained as mixtures of stereoisomers (likely *cis*-*cis*, *cis*-*trans* and *trans*-*trans*), but X-ray diffraction analysis of seven crystalline samples showed that DBAs adopt a zig-zag all-*trans* configuration in the solid state.[63a,93]



Scheme 14. Complementary strategies for the synthesis of *carbo*-*n*-butadienes **33a-j** from the **C8** triyne.

The flexible *carbo*-*n*-butadienes **33** can be compared with their rigid counterparts **31**, exhibiting the same π-conjugated chain, but included in a macrocyclic backbone. The two series are constituted by chromophoric products exhibiting comparable maximum absorption wavelengths ($552 < \lambda_{max}$ (**33**) < 669 nm and $572 < \lambda_{max}$ (**31**) < 616 nm), donor substituents and/or increase of the π-conjugation extent inducing bathochromic shifts. The general profile of the absorption spectra in these two series are quite different: while those of the cyclic *carbo*-butadienes **31** always exhibit two intense absorption bands,[61,83] those of their acyclic counterparts **33** possess a unique intense absorption band at high wavelength (Fig. 7).[63a,93] The dichromism property of some *carbo*-cyclohexadienes, which was shown to be correlated with their two-band absorption spectra, is thus significantly weakened for their acyclic counterparts, because of their different UV-vis spectral profile. These differences suggest that the dichromism of *carbo*-cyclohexadienes **31** is at least partly due to the *cisoid*-locked form of their DBA motif.

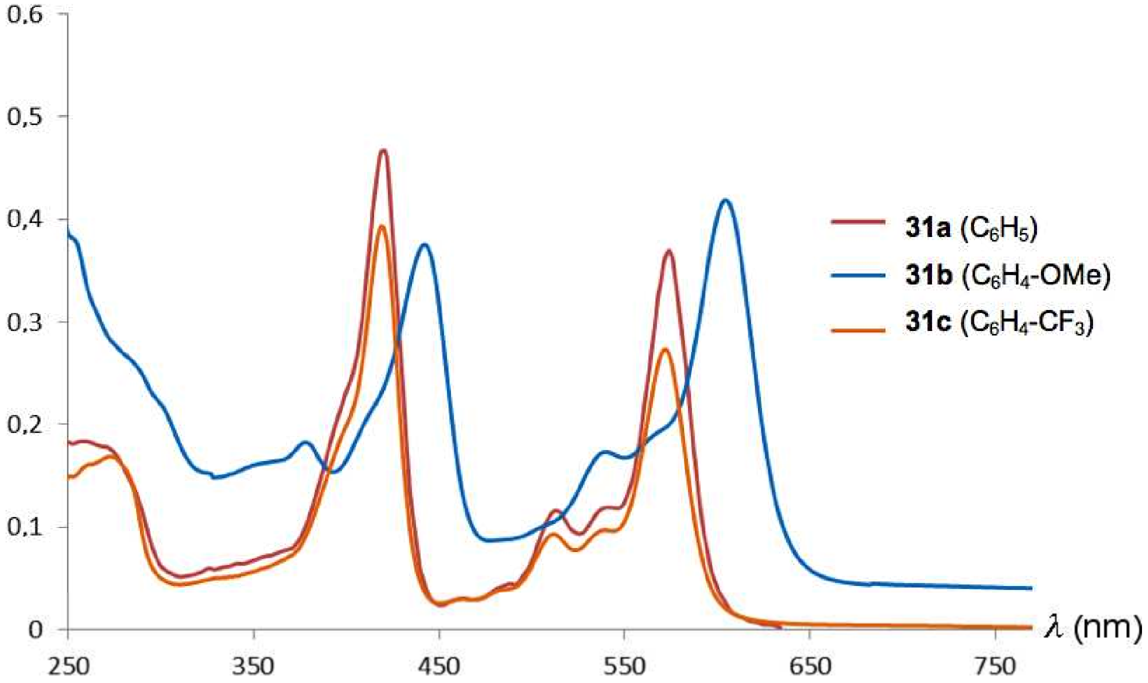
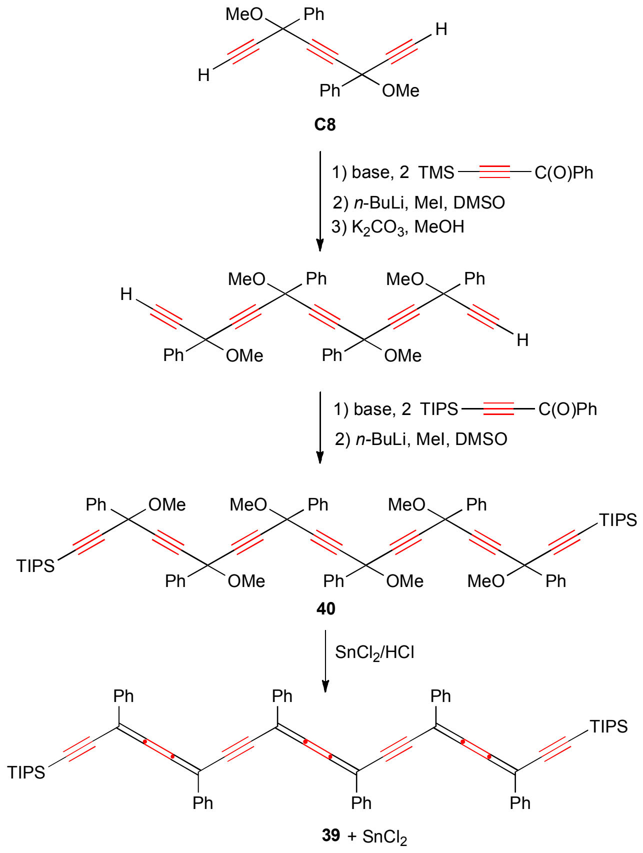


Fig. 7. UV-vis absorption spectra of the *carbo*-cyclohexadienes **33a-c** (*top*) and corresponding *carbo*-*n*-butadienes **31a-c** (*bottom*) in $CHCl_3$ solutions.

The UV-vis absorption properties of the aminophenyl-substituted *carbo*-*n*-butadienes **33f-i** were compared to those of the *carbo*-benzene counterparts **1p-s** (Fig. 3).[63a] The range of variation of the maximum absorption wavelength is twice larger in the *carbo*-*n*-butadiene series ($\Delta\lambda_{max}$ = 72 nm) than in the *carbo*-benzene series ($\Delta\lambda_{max}$ = 35 nm). This difference can be attributed to the aromaticity of the *carbo*-benzene macrocycle, making it more "insulating" and thus less sensitive to substituent effects than the acyclic DBA unit. This was confirmed by comparison of their electrochemical behavior: redox-potentials are much more sensitive to the effect of substituents in the *carbo*-*n*-butadiene series **33f-i** than in the *carbo*-benzene series **1p-s**.

2.6.3. Tributatrienyltetrayne, substituted carbo-mers of hexatriene

The perphenylated *carbo*-hexatriene **39** was synthesized using a procedure adapted from the strategy A for the preparation of *carbo*-*n*-butadienes (Scheme 15). The hexaoxyheptayne **40** precursor was first secured in five steps and 49 % overall yield from the triyne **C8**. The final reductive elimination step turned out to be tricky, because of the poor solubility and stability of the *carbo*-hexatriene target.[93a] Nevertheless, a sample of **39** in mixture with residual $SnCl_2$ could be isolated by filtration of the reaction medium at low temperature, and characterized by NMR spectroscopy and mass spectrometry. The perphenylated 1,4-PTA **39** is thus less stable than previously reported 1,2-PTAs,[89,90] likely because of the enhanced reactivity of the benzylic butatriene units in the former.



Scheme 15. Synthesis of the hexaphenyl-*carbo*-hexatriene **39**, isolated in mixture with $SnCl_2$.

Finally, comparison of the UV-vis absorption spectrum of **39** with those of shorter homologues, namely the *carbo*-*n*-butadiene **33a** and *carbo*-ethylene **34m**, evidenced a systematic bathochromic shift of *ca* 100 nm upon addition of a DAB unit to the *carbo*-oligoacetylene chain (Fig. 8).[93a]

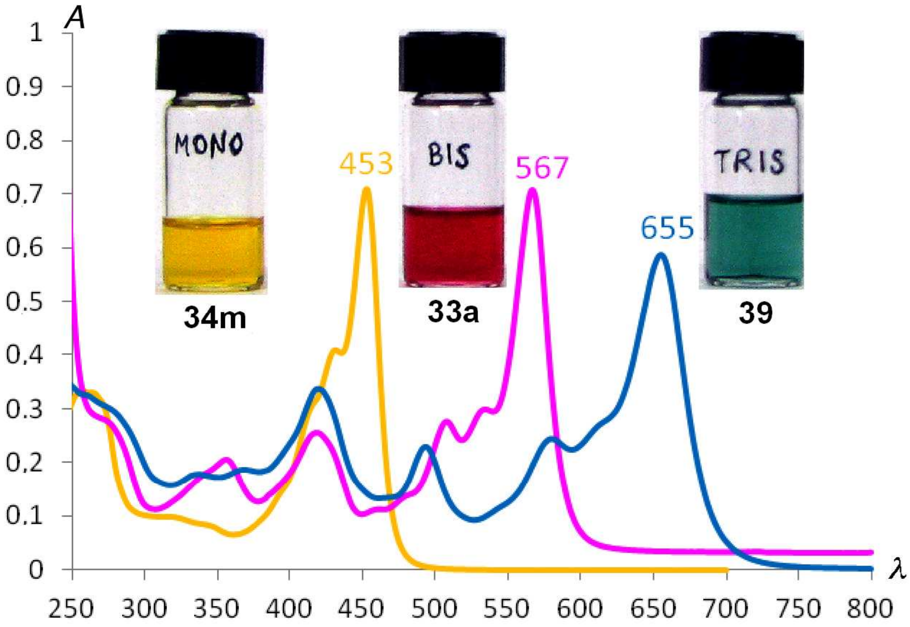


Fig. 8. Combined absorption spectra of the *carbo*-ethylene **34m**, *carbo*-*n*-butadiene **33a**, and *carbo*-hexatriene **39**, in CH_2Cl_2 solutions.

3. Polycyclic *carbo*-aromatics: *carbo*-graphene, *carbo*-graphite and fragments thereof

Joint theoretical and experimental investigations of the columnar stacking of all-*trans*-hexaethynyl-hexaoxy-[6]pericyclyne molecules (protodesilylated derivatives of **2h**, Scheme 3, section 2.2)[51] have shown how *carbo*-meric expansion can act cooperatively to enhance extended supramolecular cohesion,[94] thus defining « infinite *carbo*-materials », possibly beyond the crystal state. The concept of *carbo*-material in the structural sense is addressed below for covalent cohesion, through an overview of recent advances in the study of *carbo*-graphenes and related carbon allotropes.

3.1. *Carbo*-graphenes and *carbo*-graphites.

The C_{18} *carbo*-benzenic macrocycle and C_2 acetylenic "microcycle" (see discussion in Introduction) are aromatic building blocks and cement of two-dimensional (2D) *carbo*-graphene sheets that can be stacked to generate three-dimensional (3D) *carbo*-graphite bulk materials. In the current "*era of carbon allotropes*",[95] these still theoretical materials, called α-graphyne and α-graphitynes, respectively,[96] belong to the wide family of "graphene derivatives", which might be called "graphenoids",[97] classified by Inagaki *et al.* into sp^3-, -sp^2- or hybrid sp^2-sp^1-systems.[98]

In the all-sp^2-class, single-walled or multi-walled carbon nanotubes (SWCNT or MWCNT, respectively) may be considered as graphene rolls. Similarly, fullerenes and multifullerenes may be regarded as wrapped-up graphene pieces where the pentagonal closures of the hexagonal pattern create the positive curvature of a spherical arrangement. In the same class, graphite and amorphous carbon result from regular and turbostratic stacking of graphene sheets, respectively.[99]

The sp^3-class corresponds to diamond, and can be extended to the carbon layers of hydrogenated, fluorinated and oxidized graphenes, called respectively graphane, fluorographene and graphene oxide, and generalized the 3D counterparts, namely, graphite fluoride and graphite oxide, which are not carbon allotropes in the strict sense.

Hybrid sp^2-sp^1-systems include *carbo*-meric expansions of graphene and graphite, [3g,39-40,42], but also other graphynes and graphdiynes (Fig. 9), which are currently attracting a wide interest for their intriguing electronic, optical and mechanical properties.

The existence of graphynes was conjectured as early as 1968 by Balaban *et al.,* who estimated the relative stability of several planar and tridimensional lattices of carbon atoms using chemical graph theory.[100] It was not until the 80's, after the discovery of fullerenes,[101] that quantum chemical calculations of graphynes were undertaken. The structures, stability and electronic properties of several graphynes were first studied par Baughman *et al.* in 1987 using semi-empirical calculations (MNDO).[102] The so-called α-, β- and γ-graphynes were classified according to the numbers of carbon atoms in (i) the two smallest rings connected *via* an ethynylene link (α and β, respectively), and (ii) a third ring connected via ethynylene links to both the smallest rings in "*ortho*" position, i. e. through the shortest bond path (γ). Although the gas phase formation energy of 6,6,6-graphyne (also simply called γ-graphyne) was calculated higher (14.9 kcal/mol carbon) than the one of graphite (1.5 kcal/mol carbon). This this quite low value as compared to those of other types of graphynes, related to the occurence of a high ratio of six-membered aromatic rings, prompted chemists to take up the challenge of the synthesis of γ-graphyne, also encouraged by the existence of substructures thereof such as hexaethynylbenzene.[52,103] Today, however, research on graphyne-based materials is still in its infancy because of the remaining synthesis challenge.[104]

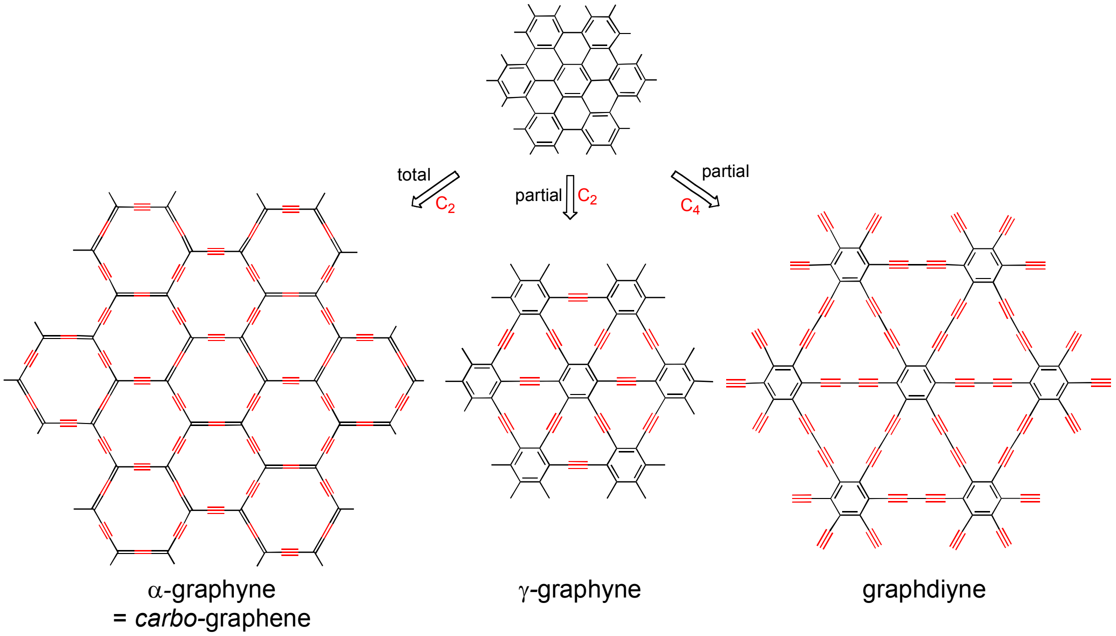


Fig. 9. Basic unit of *α*-graphyne, γ-graphyne and graphdiyne sheets.

Ten years after the first study of γ-graphyne, graphdiyne, involving diacetylenic linkages between benzene rings, was proposed by Haley *et al.* .[105] Although it was shown to be less stable than graphyne,[106] it is now available in large amount. Uniform large area films, composed of multilayer graphdiyne sheets, were indeed obtained on a copper foil by coupling reaction from hexaethynylbenzene.[107] Joint experimental and theoretical studies on graphdiyne have simultaneously flourished.[104] The incorporation of 2.5 wt% of graphdiyne in a photovoltaic device has been shown to enhance the performance by 56%.[108] Graphtriyne and graphtetrayne were also considered in few theoretical studies predicting them to be less stable than graphynes and graphdiynes.[106,109]

Structural, mechanical, optical, and conducting properties of graphyne, graphdiyne, graphone and graphane, as well as their possible synthesis routes and applications, were reviewed by Peng *et al*. in 2014.[101] The same year, the same graphene derivatives were also reviewed by Inagaki *et al.* with a focus on experimental results.[98]

γ-Graphyne is actually expected to be more efficient than graphene in applications where directionality is crucial (transistors, sensors). Flakes of γ-graphyne might thus be used as nanofillers to increase the stiffness of composite materials. Graphynes might also be used as desalinators. Adsorption of transition metals allows modulation of magnetic properties of graphyne and graphdiyne sheets.[110] Sufficient amounts of graphynes are not yet available for experimental tests of computational predictions, but a device based on graphdiyne films has been fabricated for measurement of electrical properties.[107]

The state-of-the-art in graphdiyne and graphyne research was also reviewed by A. Ivanovskii,[111] and Li *et al*.,[104] the latter authors having focused on synthesis attempts and applications of graphdiynes in optoelectronics, photovoltaics and catalysis.[104] Another review by Tang *et al.* addresses the potentialities of graphene, graphyne and graphdiyne for photovoltaic and photocatalytic applications.[112] The various ways of tuning stability, electronic and magnetic properties of graphenoids, such as functionalization, heteroatom substitution, or doping, have also been recently reviewed by Tang *et al.*[113]

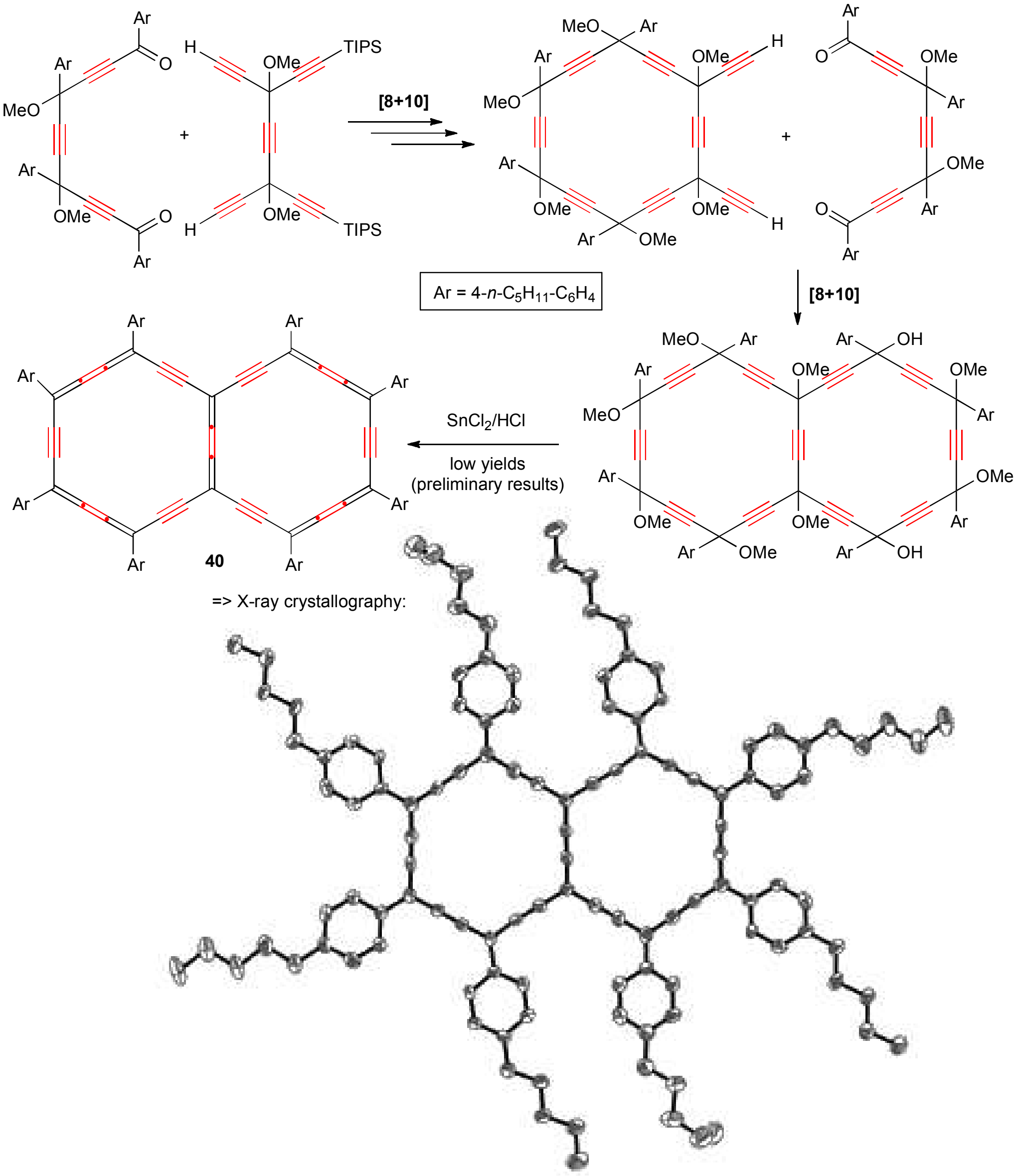
The unique conductive properties of graphene are attributed to the existence of Dirac cones in the band structure. α-, β- and 6,6,12-Graphynes are among the rare 2D materials exhibiting such Dirac cones, and are thus anticipated to possess graphene-like charge transport properties.[114] Furthermore, the carrier mobility in a 6,6,12-graphyne sheet was predicted to be larger than that prevailing in a graphene sheet.[115]

Recently, the bulk layered structure of total and partial *carbo*-mers of graphite, namely α-, and γ-graphitynes, was investigated by first-principles calculations.[96] The band gaps and band structures of these 3D-materials have been shown to depend on the number of acetylenic linkages and on the stacking mode. Most of them are graphite-like semi-metals with low charge carrier mobilities. Nevertheless, ABC-α-graphityne, which is almost as stable as AB-α-graphityne, was shown to exhibit two non-equivalent Dirac cones in its band structure. The Fermi velocities related to these Dirac cones were calculated to be just slightly lower than those reported for graphene. The band structure of bilayer α-graphyne has also been studied for six different stacking modes, two of which being found stable, one of them exhibiting a doubled Dirac cone spectrum.[116]

On this basis, many other 2D or 3D carbon graphyne-like or graphdiyne-like networks remain to be explored in view of future applications in nanomaterial sciences.

3.2. First experimental insights into the chemistry of *carbo*-benzenoids

The smallest polycyclic fragment of *carbo*-graphyne is *carbo*-naphthalene, the first derivative of which has recently obtained experimentally.[49] This first *carbo*-benzenoid **40** was synthesized through two successive [8+10] cyclization steps, followed by a $SnCl_2$-mediated reductive aromatization (Scheme 16). The *carbo*-naphthalene core being surrounded by a crown of solubilizing 4-*n*-pentylphenyl substituents, **40** could be fully characterized by spectroscopy in solution, but also by X-ray diffraction analysis of deposited single crystals. These results are being completed, in particular by ongoing theoretical studies, and will be fully described in a future report.[49] Fifty years after Nakagawa's reports on disymmetrical dehydroannulenoids,[117] and nine years after a proposition for the synthesis of structurally related *carbo*-anthracene,[42] the disclosed advances open the way to the preparation of larger *carbo*-graphyne fragments through similar multistep approaches.



Scheme 16. Preliminary results in the synthesis and characterisation of a *carbo*-naphtalene.

4. Conclusion.

The proposed concept of *carbo*-aromaticity has been at least relevant to delineate the content of this review. The fundamental topics of aromaticity and *carbo*-mers have thus met and crossed, opening new prospects in the design of highly π-electron rich and π-conjugated molecules (*e. g. carbo*-polyacetylenes). It is also noteworthy that inorganic analogues of *carbo*-benzene have been defined, such as "*iminobora*-benzenes" built by insertion of six BN azaborine units (isoelectronic to C_2) into the C-C bonds of benzene (Fig. 9).[118] The corresponding 18-membered heterocycle was shown to be aromatic, and in particular to sustain a strong diatropic ring current. More genarally, these results open the way to inorganic analogues of *carbo*-mers, namely the *iminobora*-mers, a few representatives of which have been recently studied *in silico* while remaining challenging for experimental synthesis.[119]

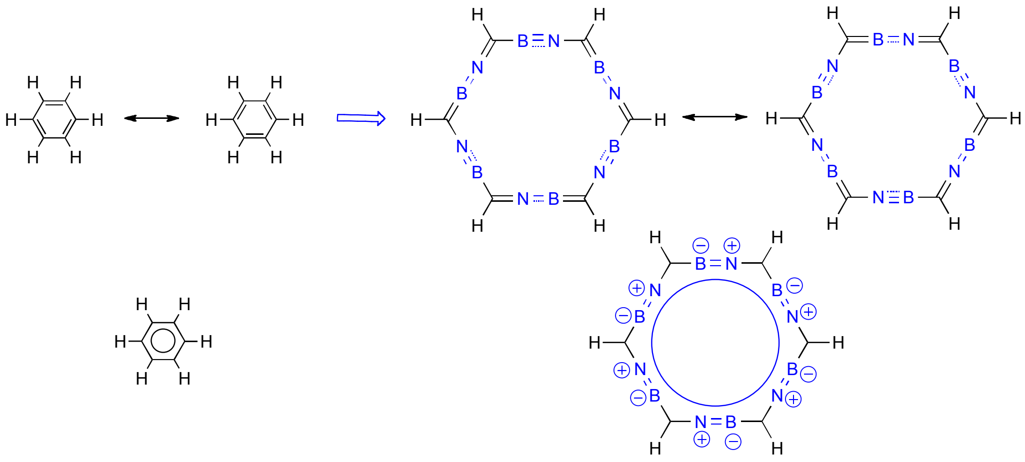


Fig. 9. Kékulé structures of *iminobora*-benzene.

The results on *carbo*-aromatics unveil new horizons in material science beyond molecular sciences, not only in terms of structures beyond graphynes and graphdiynes, *e.g.* with *carbo*-cages[120] or *carbo*-(carbon nanotubes),[51,121] but also in terms of properties (conducting electrical and linear or non-linear optical properties, *e. g.* for SMC and TPA). A future challenge will be to give significance to a concept of « *carbo*-device ».

Acknowledgements. The authors thank the Centre National de la Recherche Scientifique (CNRS) for half a teaching sabbatical for R. C. in 2014-2015, and the ANR program (ANR-11-BS07-016-01) for financial support and the doctoral fellowship of K. C. The authors are

also indebted to all the students, post-doctors, and academic collaborators having contributed to the presented work.

References and Notes

1. For a historical snapshot, see: a) L. Pauling, *J. Am. Chem. Soc.* 1931, **54**, 3570-3582; b) R. S. Mulliken, *J. Chem. Phys.* 1934, **2**, 782-793; c) L. von Szentpaly, *J. Phys. Chem. A*, Article ASAP, DOI: 10.1021/jp5084345 and citations therein.

2. See for example: a) A. Rassat, *C. R. Acad. Sci. II* 1984*,* **299**, 53-55; b) A. B. Buda and K. Mislow, *J. Am. Chem. Soc.* 1992, **114**, 6006-6012; c) R. Chauvin, *J. Phys. Chem.* 1992, **96**, 4701-4706; d) *Ibid*, 4706-47011; e) G. Gilat, *J. Math. Chem*. 1994, **15**, 197-205; f) R. Chauvin, *J. Math. Chem.* 1996, **19**, 147-174; g) M. Petitjean, *Entropy* 2003, **5**, 271-312; h) P. W. Fowler, *Symmetry Cult. Sci.* 2005*,* **16**, 321-334; i) M. Petitjean, *C. R. Chimie* 2006, **9**, 1249-1251; j) M. Pinsky, C. Dryzun, D. Casanova, P. Alemany and D. Avnir, *J. Comput. Chem.* 2008, **29**, 2712-2721; k) A. Zayit, M. Pinsky, H. Elgavi, C. Dryzun and D. Avnir, *Chirality* 2011, **23**, 17-23; l) B. Barabas and O. Fulop, *J. Math. Chem*. 2012, **50**, 1514-1520.

3. See for example: a) G. Binsch, *Naturwissenschaft*. 1973, **60**, 369-374; b) M. V. Gorelik, *Russ. Chem. Rev*. 1990, **59**, 116-133; c) V. I. Minkin, M. N. Glukhovtsev and B. Ya. Simkin, *Aromaticity and antiaromaticity: electronic and structural aspects*, Wiley, New York, 1994; d) P. v. R. Schleyer, *Pure Appl. Chem.* 1996, **68**, 209-218; e) P. v. R. Schleyer, Ed., *Aromaticity*, *Chem. Rev*., vol. **101**, ACS, 2001; f) M. Randic, *Chem. Rev*. 2003, **103**, 3449-3606; g) C. Zou, C. Lepetit, Y. Coppel and R. Chauvin, *Pure Appl. Chem.* 2006, **78**, 791-811; h) A. Stanger, *Chem. Commun.* 2009, 1939-1947; i) P. v. Ŕ. Schleyer, J. I. Wu, F. P. Cossio and I. Fernandez, *Chem.Soc.Rev*. 2014, **43**, 4909-4921; j) R. Hoffmann, *Am. Scientist* 2015, **103**, 18-21.

---

4. A. R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano and M. Szafran, *J. Am. Chem. Soc*. 1989, **111***,* 7-15.

5. For a few recent reviews and advances, see: a) M. K. Cyranski, *Chem. Rev*. 2005, **105**, 3773-3811; b) Y. Mo and P. v. R. Schleyer, *Chem. Eur. J.* 2006, **12**, 2009-2020; c) J. P. Malrieu, M. Gicquel, P. W. Fowler, C. Lepetit, J.-L. Heully and R. Chauvin, *J. Phys. Chem. A* 2008, **112**, 13203-13214; d) Z. Rashid, J. H. v. Lenthe and R. W. A. Havenith, *J. Phys. Chem. A* 2012, **116**, 4778-4788.

6. For a recent review, see: T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska and M. Palusiak, *Chem. Rev*. 2014, **114**, 6383-6422.

7. For representative recent reference, see for example: a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc*. 1996, **118**, 6317-631; b) J. A. N. F. Gomes, R. B. Mallion, *Chem. Rev*. 2001, **101**, 1349-1384; c) A. Stanger, *J. Org. Chem.* 2006*,* **71**, 883-893; d) P. W. Fowler, M. Lillington and L. P. Olson. *Pure Appl. Chem.* 2007, **79**, 969-979; e) S. Pelloni and P. Lazzeretti, *J. Phys. Chem. A* 2013, **117**, 9083-9092.

8. See for example : a) J. Poater, X. Fradera, M. Duran, M. Solà, *Chem. Eur. J.* 2003, **9**, 400-406; b) J. C. Santos, W. Tiznado, R. Contreras and P. Fuentealba, *J. Chem. Phys.* 2004, **120**, 1670-1673; c) E. Matito, M. Duran, M. Solà, *J. Chem. Phys*. 2005, **122**, 014109- ; c) J. Poater, M. Duran, M. Sola and B. Silvi, *Chem. Rev*. 2005**, 105**, 3911-3947; h) P. Bultinck, M. Rafat, R. Ponec, B. Van Gheluwe, R. Carbo-Dorca and Paul Popelier, *J. Phys. Chem*. A 2006, **110**, 7642**-**7648; b) J. Cioslowski, E. Matito, M. Solà, *J. Phys. Chem. A* 2007, **111**, 6521-6525.

9. About the reconciliation of aromaticity criteria, see for example: a) R. C. Haddon, *J. Am. Chem. Soc*. 1979, **101**, 1722-1728; b) P. v. R. Schleyer, P. K. Freeman, H. Jiao and B. Goldfuß, *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 337-34; c) C. W. Bird, *Tetrahedron* 1996,

---

52, 9945-9952; d) M. K. Cyranski, T. Krygowski, A. R. Katritzky and P. v. R. Schleyer, *J. Org. Chem*. 2002, **67**, 1333-1338; e) E. Estrada, *MATCH Commun. Math. Comput. Chem.* 2006, **56**, 331-344; f) J. Aihara, *Bull. Chem. Soc. Jpn*. 2008, **81**, 241-247; g) M. Mandado, *Theor. Chem. Acc*. 2010, **126**, 339-349; h) A. Stanger, *J. Org. Chem*. 2013, **78**, 12374-12380.

10. a) See: http://goldbook.iupac.org/A00442.html; b) V. I. Minkin, *Pure Appl. Chem*. 1999, **71**, 1919-1981.

11. For related contributions on aromaticity by Pauling, see: a) L. Pauling, G. W. Wheland, *J. Chem. Phys*. 1933, **1**, 362-374; b) L. Pauling, *J. Chem. Phys.* 1938, **4**, 673-677.

12. R. Chauvin, C. Lepetit, V. Maraval and L. Leroyer, *Pure Appl. Chem.* 2010, **82**, 769-800

13. J. Aihara, *J. Am. Chem. Soc.* 1976, **98**, 2750-2758

14. a) I. Gutman, M. Milun and N. Trinajstic, *Croat. Chem. Acta.* 1976, **48**, 87-95; b) I. Gutman, M. Milun and N. Trinajstic, *J. Am. Chem. Soc.* 1977, **99**, 1692-1704.

15. R. Chauvin, C. Lepetit, *Phys. Chem. Chem. Phys*. 2013, **15**, 3855-3860.

16. C. D. Mboyi, C. Duhayon, Y. Canac and R. Chauvin, *Tetrahedron* 2014, **70**, 4957-4970.

17. a) N. Goudard, Y. Carissan, D. Hagebaum-Reignier and S. Humbel, *HuLiS* 3.0, 2007, JDK 1.6.0_51: http://www.hulis.free.fr/; b) Y. Carissan, D. Hagebaum-Reignier, N. Goudard and S. Humbel, *J. Phys. Chem. A* 2008, **112**, 13256-13262.

18. F. A. Van-Catledge, *J. Org. Chem*. 1980, **45**, 4801-4802.

19. For a tribute to Nozoe, see for example: a) J. I. Seeman and B. P. Jonhson, *Chem. Rec.* 2015, **15**, 412-4181; b) *Chem. Rec.*, *Essays in memoriam of Nozoe*, vol. 12-15, J. I. Seeman and B. P. Jonhson Eds, Wiley, 2012-2015 ; c) *The Nozoe Autograph Books*, http://www.wiley-vch.de/util/nozoe/online.php.

20. a) J. Aihara, *J. Am. Chem. Soc*. 1977, **99**, 2048-2053; b) W. C. Herndon *J. Am. Chem. Soc*. 1982, **104** , 3541-3542.

21. See for example: a) A. L. Sargent, I. C. Hawkins, W. E. Allen, H. Liu, J. L. Sessler and C. J. Fowler, *Chem. Eur. J.* 2003, **9**, 3065-3072; b) G. Portella, J. Poater and M. Sola *J. Phys. Org. Chem.* 2005*,* **18**, 785-791; c) P. Bultinck, S. Fias and Robert Ponec, *Chem. Eur. J.* 2006, **12**, 8813-8818; d) S. Radenkovic, J. Kojic, J. Petronijevic and M. Antic, *J. Phys. Chem. A* 2014, **118**, 11591-11601.

22. a) K. Singh, A. Sharma, J. Zhang, W. Xu and D. Zhu, *Chem. Commun*. 2011, **47**, 905-907; b) M. Buhl and A. Hirsch, *Chem. Rev*. 2001, **101**, 1153-1183.

23. See for example: a) A. B. MacEven, P. v. R. Schleyer, *J. Org. Chem.* 1986, **51**, 4357-4368; b) A. A. Fokin, H. Jiao and P. v. R. Schleyer, *J. Am. Chem. Soc.* 1998**, 120***,* 9364-9365; c) C. Lepetit, B. Silvi and R. Chauvin, *J. Phys. Chem. A* 2003, **107**, 464-473; d) G. A. Burley, *Angew. Chem. Int. Ed*. 2005, **44**, 3176-3178; e) N. Toriumi, A. Muranaka, E. Kayahara, S. Yamago and M. Uchiyama, *J. Am. Chem. Soc.* 2015, **137**, 82-85.

24. a) E. Heilbronner, *Tetrahedron Lett.* 1964, **29**, 1923-1928; b) H. E. Zimmerman, *Acc. Chem. Res*. 1971, **4**, 272-280; c) H. S. Rzepa, *Chem. Rev.* 2005, **105**, 3697-3715; d) R. Herges, *Chem. Rev.* 2006, **106**, 4820-4842.

25. a) M. V. Putz, *MATCH Commun. Math. Comput. Chem*. 2010, **64**, 391-418; b) M. V. Putz, *Int. J. Mol. Sci.* 2010, **11**, 1269-1310.

26. a) D. P. Craig, *J. Chem. Soc*. **1951**, 3164-3182; b) H. J. Dauben, Jr., *Puget Sound Chemist*, 1962, **23**, 5-6; c) D. J. Bertelli, *J. Org. Chem*. 1965, **30**, 891-895.

27. B. Miller and X. Shi, *J. Am. Chem. Soc.*1987, **109***,* 579-580.

---

28. a) J. Aihara, *J. Chem. Soc. Faraday Trans*. 1995, **91**, 237-239; b) J. Aihara, M. Makino and K. Sakamoto, *J. Phys. Chem. A* 2013, **117**, 10477-10488.

29. J. S. Kudavalli, D. R. Boyd, D. Coyne, J. R. Keeffe, D. A. Lawlor, A. C. MacCormac, R. A. More O'Ferrall, S. N. Rao and N. D. Sharma, *Org. Lett*. 2010, **12**, 5550-5553.

30. S. Winstein, *J. Am. Chem. Soc.* 1959, **81**, 6524-6525.

31. See for example: a) A. T. Balaban, D. C. Oniciu, A. R. Katritzky, *Chem. Rev*. 2004, **104**, 277-2812. b) U. D. Priyakumar, G. N. Sastri, *Proc. Indian Acad. Sci. (Chem. Sci.)* 2003, **115**, 49–66; c) T. M. Krygowski, M. K. Cyranski Eds., *Aromaticity in Heterocyclic Compounds*, *Topics Heterocyclic Chem.*, vol. 19, Springer, 2009; d) J. Hey, D. Leusser, D. Kratzert, H. Fliegl, J. M. Dieterich, *Phys. Chem. Chem. Phys.* 2013, **15**, 20600-20610.

32. a) N. Horada, H. Ono, T. Nishiwaki and H. Uda, *J. Chem. Soc., Chem. Commun.* 1991, 1753-1755; b) H. S. Rzepa, K. R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 2002, 1499-1501.

33. a) Y.-L. Wu, F. Bures, P. D. Jarowski, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht and F. Diederich, *Chem. Eur. J.* 2010, **16**, 9592-9605; b) J. L. Zafra, R. C. González Cano, M. C. Ruiz Delgado, Z. Sun, Y. Li, J. T. López Navarrete, J. Wu and J. Casado, *J. Chem. Phys.* 2014, 140, 054706:1-9.

34. See for example: a) H. Masui, Coord. Chem. Rev. 2001, **219-221**, 957-992; b) F. Feixas, E. Matito, J. Poater and M. Solà, *WIREs Comput. Mol. Sci.* 2013, **3**, 105-122.

35. See for example : a) K. K. Zborowski, M. Sola, J.Poater and L. M. Proniewicz, *J. Phys. Org. Chem*. 2011, **24**, 499-506; b) E. Kleinpeter and A. Koch, Phys. Chem. Chem. Phys., 2011, 13, 20593–20601.

36. For discussion and examples, see: a) D. Lloyd and D. R. Marshall, *Angew. Chem. Int. Ed. Engl*. 1972, **11**, 404-408; b) J. Aihara, *Bull. Chem. Soc. Jpn*. 1987, **60**, 2268-2270; c) M.

Palusiak and T. M. Krygowski, C*hem. Eur. J.* 2007, **13**, 7996-8006; d) H. B. Hu, X. Y. Chen, S. Deng, F. Cai, Y. Q. Sun, Y. P. Chen, *J. Mol. Struct*. 2012, **1010**, 67-72.

37. P. W. Fowler, S. Cotton, D. Jenkinson, W. Myvold, W. H. Bird, *Chem. Phys. Lett.* 2014, **597**, 30-35.

38. a) A. R . Ubbelohde, *Nature* 1957, 180, 380; b) J. Yoo, H.-J. Kim, H.-J. Kim and C.-H. Lee, *J. Porphyrins Phthalocyanines* 2011, **15**, 674–677.

39. a) R. Chauvin, *Tetrahedron Lett*. 1995, **36**, 397-400; b) V. Maraval and R. Chauvin, *New J. Chem*. 2007, **31**, 1853−1873

40. R. Chauvin, *Tetrahedron Lett*. 1995, **36**, 401-404.

41. a) Y. Kuwatani, N. Watanabe and I. Ueda, *Tetrahedron Lett*. 1995, **36**, 119-122; b) R. Suzuki, H. Tsukuda, N. Watanabe, Y. Kuwatani and I. Ueda, *Tetrahedron* 1998, **54**, 2477-2496.

42. V. Maraval and R. Chauvin, *Chem. Rev*. 2006, **106**, 5317-5343.

43. K. Cocq, V. Maraval, N. Saffon-Merceron and R. Chauvin, *Chem. Rec*. 2015, **15**, 347-361.

44. For references on pericyclynes see: a) L. T. Scott, G. J. DeCicco, J. L. Hyunn and G. Reinhardt, *J. Am. Chem. Soc*. 1983, **105**, 7760-7761; b) L. T. Scott, G. J. DeCicco, J. L. Hyunn and G. Reinhardt, *J. Am. Chem. Soc.* 1985, **107**, 6546–6555; c) K. N. Houk, L. T. Scott, N. G. Rondan, D. C. Spelleyer, G. Reinhardt, J. L. Hyunn, G. J. DeCicco, R. Weiss, M. H. M. Chen, L. S. Bass, J. Clardy, F. S. Jorgensen, T. A. Eaton, V. Sarkozi, C. M. Petit, L. Ng and K. D. Jordan, *J. Am. Chem. Soc*. 1985, **107**, 6556-6562. For references on hexaoxy[6]pericyclynes see: d) C. Saccavini, C. Tedeschi, L. Maurette, C. Sui-Seng, C. Zou, M. Soleilhavoup, L. Vendier and R. Chauvin, *Chem.–Eur. J.* 2007, **13**, 4895-4913; e) L. Leroyer, C. Zou, V. Maraval and R. Chauvin, *C. R. Chimie* 2009, **12**, 412-419.

---

45. C. Saccavini, C. Sui-Seng, L. Maurette, C. Lepetit, S. Soula, C. Zou, B. Donnadieu and R. Chauvin, *Chem.–Eur. J.* 2007, **13**, 4914-4931.

46. For recently reported synthesis of **4c**, see: a) H. Wang, Y. Liang, H. Xie, L. Feng, H. Lu and S. Feng, *J. Mater. Chem. C*, 2014, **2**, 5601-5606; for **4d**, see: b) T. Matsuda and N. Muria, *Org. Biomol. Chem*. 2013, **11**, 3424-3427; for **4e**, see: c) N. Yoshikai, H. Mashima and E. Nakamura, *J. Am. Chem. Soc*. 2005, **125**, 17978-17979; d) V. A. Rassadin, E. Nicolas and Y. Six, *Chem. Commun*. 2014, **50**, 7666-7669.

47. C. Kübel, K. Eckhardt, V. Enkelmann, G. Wegner and K. Müllen, *J. Mater. Chem.* 2000, **10**, 879-886.

48. R. Liu, D. Wu, X. Feng and K. Müllen, *J. Am. Chem. Soc*. 2011, **133**, 15221-15223.

49. K. Cocq, C. Poidevin, C. Lepetit, N. Saffon-Merceron, V. Maraval and R. Chauvin, *manuscript in preparation*.

50. C. Zou, C. Duhayon, V. Maraval and R. Chauvin, *Angew. Chem. Int. Ed.* 2007, **46**, 4337-4341.

51. C. Lepetit, C. Zou and R. Chauvin, *J. Org. Chem*. 2006, **71**, 6317-6324.

52. R. Diercks and K. P. C. Vollhardt, *J. Am. Chem. Soc.* 1986, **108**, 3150-3152.

53. S. Nobusue, Y. Mukai, Y. Fukumoto, R. Umeda, K. Tahara, M. Sonoda and Y. Tobe, *Chem. Eur. J.* 2012, **18**, 12814-12824.

54. C. Lepetit, P. Lacroix, V. Peyrou, C. Saccavini and R. Chauvin, *J. Comput. Methods Sci. Eng*. 2004, **4**, 569-588.

55. K. Nakatani, P. G. Lacroix, C. Saccavini and R. Chauvin, *unpublished results*.

56. C. Saccavini, Ph.D. Dissertation, Université Paul Sabatier, Toulouse, Oct. 24, 2004.

57. I. Baglai, M. de Anda-Villa, R. M. Barba-Barba, G. Ramos-Ortíz, C. Poidevin, V. Maraval, C. Lepetit, N. Saffon-Merceron, J.-L. Maldonado and R. Chauvin, *Chem.-Eur. J., manuscript under revision.*

58. O. Mongin, L. Porrès, M. Charlot, C. Katan and M. Blanchard-Desce, *Chem.–Eur. J.* 2007, **13**, 1481-1498.

59. a) M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron*. 1990, **26**, 760-769; b) *Characterization Techniques and Tabulations for Organic Nonlinear Materials*, (Eds : H. G. Kuzyk and C. W. Dirk), M. Dekker, New York, NY, 1998.

60. J. M. Kauffman, C. J. Kelley, A. Ghiorghis, E. Neister and L. Armstrong, *Laser Chem*. 1998, **8**, 335-348.

61. L. Leroyer, C. Lepetit, A. Rives, V. Maraval, N. Saffon-Merceron, D. Kandaskalov, D. Kieffer and R. Chauvin, *Chem.–Eur. J.* 2012, **18**, 3226-3240.

62. 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).

63. a) A. Rives, I. Baglai, V. Malytskyi, V. Maraval, N. Saffon-Merceron, Z. Voitenko and R. Chauvin, *Chem. Commun*. 2012, **48**, 8763-8765; b) I. Baglai, V. Maraval, C. Bijani, N. Saffon-Merceron, Z. Voitenko, Y. M. Volovenko and R. Chauvin, *Chem. Commun*. 2013, **49**, 8374-8376.

64. I. Baglai, V. Maraval, Z. Voitenko, Y. Volovenko and R. Chauvin, *French-Ukr. J. Chem*. 2013, **1**, 48-53.

65. Only patents were reported for **17**, but **16** has been the subject of publications: a) K.-R. Wee, Y.-J. Cho, S. Jeong, S. Kwon, J.-D. Lee, I.-H. Suh and S. O. Kang, *J. Am. Chem. Soc*. 2012, **134**, 17982-17990; b) L.-L. Zhang, H. Ren, Y. Zhang, R.-S. Wang and X.-M. Pan, *Theor. Chem. Acc*. 2013, **132**, 1302, 1-11.

66. See for example: a) Q. Li, K. Liu, H. Zhang, Z. Du, X. Wang and F. Wang, *ACS Nano*, 2009, **3**, 3861-3868; b) P. Moreno-García, M. Gulcur, D. Zsolt Manrique, T. Pope, W. Hong,

---

V. Kaliginedi, C. Huang, A. S. Batsanov, M. R. Bryce, C. Lambert and T. Wandlowski, *J. Am. Chem. Soc*. 2013, **135**, 12228-12240; c) Z. Li, M. Smeu, M. A. Ratner and E. Borguet, *J. Phys. Chem. C*, 2013, **117**, 14890-14898.

67. B. Xu and N. J. Tao, *Science* 2003, **301**, 1221-1223.

68. a) F. Chen, X. Li, J. Hihath, Z. Huang and N. J. Tao, *J. Am. Chem. Soc.* 2006, **128**, 15874-15881; b) X. Xing, T.-H. Park, R. Venkatramani, S. Keinan, D. N. Beratan, M. J. Therien and E. Borguet, *J. Am. Chem. Soc*. 2010, **132**, 7946-7956.

69. Z. Li, M. Smeu, A. Rives, V. Maraval, R. Chauvin, M. A. Ratner and E. Borguet, *Nature Commun.* 2015, **6**, 6321.

70. As the conductance is known to decrease exponentially *vs* the length of the molecular junction, **1p** is a much more efficient single molecular conductor than its competitors of similar or shorter length. See for example ref 27a.

71. Z. Li and E. Borguet, *J. Am. Chem. Soc.* 2012, **134**, 63-66.

72. I. Diez-Perez, Z. H. Li, J. Hihath, J. H. Li, C. Y. Zhang, X. M. Yang, L. Zang, Y. J. Dai, X. L. Feng, K. Muellen and N. J. Tao, *Nature Commun*. 2010, 1-5.

73. Y. Sakaguchi and F. W. Harris, *Polym. J.* 1992, **24**, 1147-1154.

74. F. W. Harris, Y. Sakaguchi, M. Shibata and S. Z. D. Cheng, *High Perform. Polym*. 1997, **9**, 251-261.

75. See for example: a) L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen and M. L. Steigerwald, *Nature* 2006, **442**, 904-907; b) J. R. Quinn, F. W. Foss Jr., L. Venkataraman and R. Breslow, *J. Am. Chem. Soc.* 2007, **129**, 12376-12377; c) S. Y. Quek, H. J. Choi, S. G. Louie and J. B. Neaton, *Nano Lett.* 2009, **9**, 3949-3953; d) T. Kim, H. Vazquez, M. S. Hybertsen and L. Venkataraman, *Nano Lett*. 2013, **12**, 3358-3364.

76. a) Y.-L. Wu, F. Bures, P. D. Jarowski, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht and F. Diederich, *Chem.–Eur. J.* 2010, **16**, 9592-9605; b) J. L. Zafra, R. C. González Cano,

M. C. Ruiz Delgado, Z. Sun, Y. Li, J. T. López Navarrete, J. Wu and J. Casado, *J. Chem. Phys*. 2014, **140**, 054706:1-9.

77. Y.-L. Wu, F. Tancini, W. B. Schweizer, D. Paunescu, C. Boudon, J.-P. Gisselbrecht, P. D. Jarowski, E. Dalcanale and F. Diederich, *Chem. Asian J*. 2012, **7**, 1185-1190.

78. K. Cocq, V. Maraval, N. Saffon-Merceron, A. Saquet, C. Poidevin, C. Lepetit and R. Chauvin, *Angew. Chem. Int. Ed*. 2015, **54**, 2703-2706.

79. a) B. J. Dahl and N. S. Mills, *J. Am. Chem. Soc*. 2008, **130**, 10179-10186; b) J. Fabian, *Dyes Pigments* 2010, **84**, 36-53.

80. M. Gholami, M. N. Chaur, M. Wilde, M. J. Ferguson, R. McDonald, L. Echegoyen and R. R. Tykwinski, *Chem. Commun*. 2009, 3038-3040.

81. E. Weber, S. Nitsche, A. Wierig and I. Csöregh, *Eur. J. Org. Chem*. 2002, 856–872.

82. a) T. M. Krygowski and B. T. Stępień, *Chem. Rev*. 2005, **105**, 3482-3512; b) T. M. Krygowski, M. A. Dobrowolski, M. K. Cyrański, W. P. Oziminski and P. Bultinck, *Comput. Theor. Chem*. 2012, **984**, 36–42.

83. a) A. Rives, I. Baglai, C. Barthes, V. Maraval, N. Saffon-Merceron, Z. Voitenko, Y. Volovenko and R. Chauvin, *Chem. Sci*. 2015, **6**, 1139-1149; b) O. Lozynskyi, C. Barthes, A. Rives, V. Maraval, Z. Voitenko and R. Chauvin, *French Ukr. J. Chem.* 2015, **3**, 46-52.

84. C. Barthes, A. Rives, V. Maraval, E. Chelain, T. Brigaud and R. Chauvin, *French Ukr. J. Chem.* 2015, **3**, 60-65.

85. For references on di- and tetra-alkynylbutatrienes see: a) J.-D. van Loon, P. Seiler and F. Diederich, *Angew. Chem. Int. Ed*. 1993, **32**, 1187-1189; b) A. Auffrant, F. Diederich, C. Boudon, J.-P. Gisselbrecht and M. Gross, *Helv. Chim. Acta* 2004, **87**, 3085-3105; c) A. Auffrant, B. Jaun, P. D. Jarowski, K. N. Houk and F. Diederich, *Chem.–Eur. J*. 2004, **10**, 2906-2911; d) V. Maraval, L. Leroyer, A. Harano, C. Barthes, A. Saquet, C. Duhayon, T. Shinmyuzo and R. Chauvin, *Chem.–Eur. J*. 2011, **17**, 5086-5100; e) L. Leroyer, V. Maraval and R. Chauvin, *Chem. Rev*. 2012, **112**, 1310-1343.

---

86. a) D. Naumann, B. Wilkes and J. Kischkewitz, *J. Fluorine Chem*. 1985, **30**, 73-87; b) V. A. Grinberg, S. A. Lundgren, S. R. Sterlin and E. I. Mysov, *Russ. Chem. Bull*. 1997, **46**, 1131-1135.

87. B. C. Ahvazi and D. S. Argyropoulos, *J. Agric. Food Chem*. 1996, **44**, 2167-2175.

88. a) T. M. Krygowski and B. T. Stępień, *Chem. Rev*. 2005, **105**, 3482-3512; b) M. K. Cyranski, *Chem. Rev*. 2005, **105**, 3773-3811.

89. M. Schreiber, J. Anthony, F. Diederich, M. E. Spahr, R. Nesper, M. Hubrich, F. Bommeli, L. Degiorgi, P. Wachter, P. Kaatz, C. Bosshard, P. Günter, M. Colussi, U. W. Suter, C. Boudon, J.-P. Gisselbrecht and M. Gross, *Adv. Mater*. 1994, **6**, 786-790.

90. a) J. F. Nierengarten, D. Guillon, B. Heinrich and J. F. Nicoud, *Chem. Commun*. 1997, 1233-1234; b) J. Xiao, M. Yang, J. W Lauher and F. W. Fowler, *Angew. Chem. Int. Ed*. 2000, **39**, 2132-2135; c) F. Diederich, *Chem. Commun*. 2001, 219-227 and references therein; d) A. P. H. J. Schenning, J.-D. Arndt, M. Ito, A. Stoddart, M. Schreiber, P. Siemsen, R. E. Martin, C. Boudon, J.-P. Gisselbrecht, M. Gross, V. Gramlich and F. Diederich, *Helv. Chim. Acta* 2001, **84**, 296-334; e) N. F. Utesch, F. Diederich, C. Boudon, J. P. Gisselbrecht and M. Gross, *Helv. Chim. Acta* 2004, **87**, 698-718; f) J. F. Nierengarten, *Helv. Chim. Acta* 2004, **87**, 1357-1367.

91. P. D. Jarowski, F. Diederich and K. N. Houk, *J. Phys. Chem. A* 2006, **110**, 7237-7246.

92. a) P. Fritsch, *Justus Liebigs Ann. Chem*. 1894, **279**, 319; b) W. P. Buttenberg, *Justus Liebigs Ann. Chem*. 1894, **279**, 324; c) H. Wiechell, *Justus Liebigs Ann. Chem.* 1894, **279**, 337. For recent uses of the FBW rearrangement see for example: d) Y. Morisaki, T. Luu and R. R. Tykwinski, *Org. Lett*. 2006, **8**, 489-692; e) T. Luu, Y. Morisaki, N. Cunningham and R. R. Tykwinski, *J. Org. Chem*. 2007, **72**, 9622-9629.

---

93. a) A. Rives, V. Maraval, N. Saffon-Merceron and R. Chauvin, *Chem.–Eur. J.* 2012, **18**, 14702-14707; b) A. Rives, V. Maraval, N. Saffon-Merceron and R. Chauvin, *Chem.–Eur. J.* 2014, **20**, 483-492.

94. O. V. Shishkin, R. I. Zubatyuk, V. V. Dyakonenko, C. Lepetit and R. Chauvin, *Phys. Chem. Chem. Phys.* 2011, **13**, 6837-6848.

95. A. Hirsch, *Nat. Mater.* 2010, **9**, 868–871.

96. J.-M. Ducéré, C. Lepetit and R. Chauvin, *J. Phys. Chem. C* 2013, **117**, 21671–21681.

97. M. Pumera, *Electrochem. Commun*. 2013, **36**, 14-18.

98. M. Inagaki and F. Kang, *J. Mater. Chem. A* 2014, **2**, 13193–13206.

99. a) M. Inagaki, in « *New Carbons - Control of Structure and Functions* », Elsevier, 2000; b) M. Inagaki and F. Kang, in *Carbon Materials Science and Engineering - From Fundamentals to Applications* », Tsinghua University Press, 2006.

100. A.T. Balaban, C. C. Rentia and E. Ciupitu, *Rev. Roum. Chim.* 1968, **13**, 231-247.

101. Q. Peng, A. K. Dearden, J. Crean, L. Han, S. Liu, X. Wen and S. De, *Nanotechnol. Sci. Applications* 2014, **7**, 1–29.

102. R. H. Baughman, H. Eckhardt, M. Kertesz *J. Chem. Phys.* 1987, **87**, 6687–6699.

103. R. Diercks, J. C. Armstrong, R. Boese and K. P. C. Vollhardt, *Angew. Chem. Int. Ed. Engl.,* 1986, **25**, 268–269.

104. Y. Li, L. Xu, H. Liu and Y. Li, *Chem. Soc. Rev.* 2014, **43**, 2572-2586.

105. M. M. Haley, S. C. Brand and J. J. Pak, *Angew. Chem. Int. Ed. Engl.,* 1987, **36**, 836–838.

106. N. Narita, S. Nagai, S. Suzuki and K. Nakao, *Phys. Rev. B: Condens. Matter Mater. Phys*., 1998, **58**, 11009.

---

107. G. X. Li, Y. L. Li, H. B. Liu, Y. B. Guo, Y. J. Li and D. B. Zhu, *Chem. Commun.* 2010, **46**, 3256–3258.

108. H. L. Du, Z. B. Deng, Z. Y. Lü, Y. H. Yin, L. L. Yu, H. Wu, Z. Chen, Y. Zou, Y. S. Wang, H. B. Liu and Y. L. Li, *Synth. Met.* 2011, **161**, 2055–2057.

109. M. Bartolomei, E. Carmona-Novillo, M. I. Hernández, J. Campos-Martínez, F. Pirani, G. Giorgi and K. Yamashita, *J. Phys. Chem. Lett.* 2014, **5**, 751−755.

110. J. He, S. Y. Ma, P. Zhou, C. X. Zhang, C. He and L. Z. Sun, *J. Phys. Chem. C* 2012, **116**, 26313−26321.

111. A. L. Ivanovskii, *Prog. Solid State Chem.* 2013, **41**, 1–19.

112. H. Tang, C. M. Hessel, J. Wang, N. Yang, R. Yu, H. Zhao and D. Wang, *Chem. Soc. Rev.* 2014, **43**, 4281–4299.

113. Q. Tang, Z. Zhou and Z. Chen, *Nanoscale* 2013, **5**, 4541-4583.

114. J. Wang, S. Deng, Z. Liu, Z. Liu, *arXiv.org, e-Print Archive, Condensed Matter* 2014, 1-41, arXiv:1410.5895v1

115. a) J. Chen, M. Long, I. Tang, D. Wang and Z. Shuai, *J. Phys. Chem. Lett.* 2013, **4**, 1443–1448; b) Z. Shuai, D. Wang, Q. Peng and H. Geng, *Acc. Chem. Res.* 2014, **47**, 3301–3309.

116. O. Leeneerts, B. Partoens and F. Peeters, *Appl. Phys. Lett.* 2013, **103**, 013105.

117. M. Iyoda, F. Ogura, S. Akiyama and M. Nakagawa, *Chem. Lett*. 1983, 1883-1886.

118. A. Soncini, P. W. Fowler, I. Cernusak and E. Steiner, *Phys. Chem. Chem. Phys.* 2001, **3**, 3920–3923.

119. S. Jalifea, M. Audiffred , R. Islas, S. Escalante, S. Pan, P. K. Chattaraj and G. Merino, *Chem. Phys. Lett.* 2014, **610-611**, 209–212.

---

120. (a) S. M. Bachrach and D. W. Demoin, *J. Org. Chem.* 2006, **71**, 5105–5116. (b) P. D. Jarowski, F. Diederich and K. N. Houk, *J. Org. Chem.* 2005, **70**, 1671–1678. (c) J. M. Azpiroz, R. Islas, D. Moreno, M. A. Fernández-Herrera, S. Pan, P. K. Chattaraj, G. Martínez-Guajardo, J. M. Ugalde, and Gabriel Merino, *J. Org. Chem.* 2014, **79**, 5463–5470.

121. W. Liu, Y. Li and Y.Huang *J. Phys. Chem. Solids.* 2011, **72**, 299–306.