

CHEMISTRY A European Journal





ACES

WILEY-VCH

Steric/ π -electronic insulation of the *carbo*-benzene ring: dramatic effects of *tert*-butyl *vs* phenyl crowns on geometric, chromophoric, redox and magnetic properties

Dymytrii Listunov,^[a,b] Carine Duhayon, Albert Poater,^[c] Serge Mazères,^[d] Alix Saquet,^[a,b] Valérie Maraval,^{*[a,b]} Remi Chauvin^{*[a,b]}

Abstract: Hexa-*tert*-butyl-*carbo*-benzene C₁₈^tBu₆ and three phenylated counterparts $C_{18}^{t}Bu_mPh_{6-m}$ (m = 4, 2) have been synthesized. The peralkylated version (m = 6) provides experimental access to intrinsic features of the insulated C18 core independently from the influence of π -conjugated substituent. Over the series, structural, spectroscopical and electrochemical properties are compared with those of the hexaphenylated reference (m = 0). Anchoring ^tBu substituents at the C₁₈ macrocycle is shown to enhance stability and solubility, and to dramatically modify UV-vis absorption and redox properties. Whereas all the carbo-benzenes reported hitherto were obtained as dark-reddish/greenish solids, crystals and solutions of $C_{18}^{t}Bu_{6}$ happen to be yellow (λ_{max} = 379 nm vs 472 nm for $C_{18}Ph_6$). By comparison to $C_{18}Ph_6$, reduction of $C_{18}^{t}Bu_6$ remains reversible but occurs at a twice higher absolute potential ($E_{1/2} = -1.36$ V vs -0.72 V). Systematic X-ray diffraction analyses and DFT calculations show that the C_{18} ring symmetry is the nearest to D_{6h} for m = 6, indicating a maximum geometrical aromaticity. According to calculated nucleus independent chemical shifts, the macrocyclic magnetic aromaticity is also found to be maximum for $C_{18}^{t}Bu_{6}$: NICS(0) = -17.2 ppm, vs -18.0 ± 0.1 ppm for the theoretical references $C_{18}H_6$ and $C_{18}F_6$, and -13.5 ppm for $C_{18}Ph_6$. Accurate correlations of NICS(0) with experimental or calculated maximum UVvis absorption wavelength λ_{max} and chemical hardness $\eta = E_{LUMO}$ - $E_{\rm HOMO}$ are evidenced.

- [a] Dr. D. Listunov, Dr. C. Duhayon, Dr. A. Saquet, Dr. V. Maraval, Prof. R. Chauvin
 CNIPS, L.CC. (Leberate in de Chimie de Capacitization). 205 route de la
- CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4, France. E-mail: <u>vmaraval@lcc-toulouse.fr</u>; <u>chauvin@lcc-toulouse.fr</u>
- [b] Dr. D. Listunov, Dr. C. Duhayon, Dr. A. Saquet, Dr. V. Maraval, Prof. R. Chauvin Université de Tauleure, URD, ICT ED 0500, 440 surte de Nacharage
- Université de Toulouse, UPS, ICT-FR 2599, 118 route de Narbonne, 31062 Toulouse Cedex 9, France. c] Dr. A. Poater
- [c] Dr. A. Poater Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Campus Montilivi, 17071 Girona, Catalonia, Spain
- [d] Dr. S. Mazères UMR CNRS 5089, IPBS (Institut de Pharmacologie et de Biologie Structurale), 205 route de Narbonne, 31077 Toulouse cedex, France.

Supporting information for this article is given via a link at the end of the document. It includes experimental synthesis procedures and characterization data for all new compounds, crystallographic tables and figures, voltammograms, NMR spectra, and detailed computational data based on DFT-optimized Cartesian coordinates of main compounds discussed in the main text.

Introduction

Within the family of cumulene-containing conjugated cyclic hydrocarbons,^[1a] carbo-benzenes^[1b,c] display particular optical,^[2] electrical,^[3] magnetic,^[4] or mesogenic^[5] properties, that can be a priori attributed to their common C18 core, combining unique geometrical and π -electronic features. In spite of a 4n+2 π_z electron count, however, the moderate energetic aromaticity of the C_{18} ring (ca one third of the C_6 ring of benzene)^[6] enables conjugation with π -unsaturated substituents. All the carbobenzene cores reported to date are actually substituted by either six alkynyl groups (as in 1)^[7] or at least three aryl groups (as in 2),^[8] most of them with four phenyl groups (as in 3),^[1b] and up to six in 4 (Fig. 1).^[8,9] The outer π -conjugation is evidenced by low dihedral angles φ between the C₁₈ ring mean plane and the mean planes of the aryl substituents ($0 \le \varphi < 20^\circ$). No more than two or three of the remaining substituents can be H or alkyl groups (e.g. in 2a-b^[8] or 3a-c),^[10,11] and since the first unsuccessful attempt at synthesis of the unsubstituted carbo-benzene $C_{18}H_{61}^{[12]}$ no experimental example of a π -isolated C₁₈ core has been at disposal for appraising its intrinsic electronic properties. With the additional requirement of preventing π - π stacking of C₁₈ rings, the challenge is here addressed by decorating the macrocycle with a crown of six *tert*-butyl substituents. Beyond the $C_{18}^{t}Bu_{6}$ target 5, partially phenylated congeners C₁₈^tBu_mPh_{6-m} (6, 7, 8 in Scheme 1) are also envisaged. Comparison with the hexaphenylated reference 4 (m = 0) is ultimately envisaged with the view to appraising the incremental effect of outer conjugation with phenyl groups, e. g. by UV-vis absorption spectroscopy. All the known carbo-benzenes are indeed highly chromophoric, with a UV-vis profile reminiscent of the UV-vis profile of porphyrins:^[2,13] one main absorption band and smaller bands at higher wavelengths can be compared with the Soret and Q bands of porphyrins, respectively. Furthermore, the UV-vis spectra of carbo-benzenes is also interpretable through the Gouterman four-orbital model devised for porphyrins.^[14] The maximum absorption wavelengths λ_{max} of all the known *carbo*-benzenes with a single C₁₈ ring are in the range 472 ± 48.5 nm, the mean value corresponding to the λ_{max} value of C₁₈Ph₆, **4** (λ_{max} = 472 nm).^[8,9] This range of variation is twice larger than the one reported for porphyrins (420 ± 25 nm), whatever the nature and position of the substituents on the tetrapyrolic C₂₀ macrocycle.^[15] This difference indicates that the C_{18} carbo-benzene core is more prone to external π delocalization than the $C_{20}N_4$ porphine core, thus revealing a lower aromatic character of the former. Remarkably, the mean value at 420 nm corresponds to the λ_{max} value of the meso-

FULL PAPER

tetraphenyl derivative **P1**, to be compared with the hexaphenyl derivative **4** in the *carbo*-benzene series.



Figure 1. Examples of know *carbo*-benzene derivatives and related porphyrins, and the target 5.

The lowest known maximum absorption wavelengths amongst *carbo*-benzenes with a single C₁₈ ring were measured for the triaryl representatives **2a** and **2b** ($\lambda_{max} = 424$ and 427 nm),^[8b] while the highest value was recorded for the π -donor-substituted hexaaryl *carbo*-benzene **3d** ($\lambda_{max} = 521$ nm).^[3,16] A first open issue for the target **5** is thus whether the π -insulating effect of the six ¹Bu groups will overcome their σ -donating inductive effect that could parallel the π -donating mesomeric effect of the two 4-NMe₂C₆H₄ groups of **3d**. Furthermore, the target series C₁₈'Bu_mPh_{6-m} lends itself to systematic investigations of fluorescence, structural and electrochemical properties. The variation of electronic and magnetic properties *vs* m is also addressed by DFT calculations below.

The synthesis of **5**, **6**, **7** and **8** has been challenged through an adapted [8+10] macrocyclization route to their respective [6]pericyclynediol precursors **9**, **10**, **11** and **12** (Scheme 1).^[17] The common di-*tert*-butylated synthon **13** was envisaged by a method previously described for the preparation of the di-phenylated version **14**.^[18]



Scheme 1. Retrosynthetic [8+10] route to the fully and partially *tert*-butyl-substituted *carbo*-benzenes from the common precursor **13**.

Results and Discussion

1. Synthesis of the di-tert-butyl-triyne C₈ precursor 13

The preparation of **13** was initiated from the ketone **15**, obtained in quantitative yield by AlCl₃-promoted acylation of bistrimethylsilylacetylene with pivaloyl chloride (Scheme 2).^[19,20] Reaction of **15** with ethynylmagnesium bromide gave the diynol **16** in 80 % yield. Selective O-methylation of **16** by treatment with one equivalent of *n*-BuLi and MeI led to **17** with 92 % yield. Deprotonation of **17** with EtMgBr followed by addition to **15** gave the triynol **18**, which was readily O-methylated to the diether **19**. Subsequent proto-desilylation with K₂CO₃/MeOH afforded the triyne **13**, with 85 % yield from **19**, and 42 % overall yield over six steps from pivaloyl chloride.

A more straightforward method consisted in the direct addition of the terminal diyne **16** to the ketone **15** in the presence of an excess of LiHMDS, giving the triynediol **20** with 87 % yield. Subsequent double O-methylation and C-desilylation allowed access to **13** with 58 % yield over four steps only. This shorter procedure was also applied in the preparation of the phenylated triyne **14**, widely used for the synthesis of *carbo*-benzenes of type **3** (Figure 1).^[1b,10,11,13,18] The triynes **18-20** and **13** were obtained as quasi-statistical mixtures of stereoisomers, and used as such in the next steps. Structures were confirmed by X-ray diffraction (XRD) analysis of single crystals of *rac*-**16**, *rac-erythro* (*R**,*R**)-**18** and *meso*-**13** spontaneously resolved by deposition from DCM/pentane solutions (Supporting Information Figure S.3.1).^[21]

FULL PAPER



Scheme 2. Synthesis of the triyne 13, common precursor of the target carbo-benzenes 5-8 (Scheme 1).

2. Synthesis of dialdehyde and diketone C₁₀ precursors

[8+10] Macrocyclization from the C₈ triyne **13** was first envisaged with the *tert*-butylated C₁₀ dialdehyde **21** (R² = H in Scheme 1). Following a procedure used in the phenylated series from the triyne **14**,^[17c,18] **13** was first deprotonated with two equivalents of *n*-BuLi before addition to *para*-formaldehyde, and the resulting diol **22** was oxidized with IBX to give **21** with 68 % yield over two steps (Scheme 3).

As an alternative dielectrophile, the diketone **23** was prepared in one step through "pseudo-Sonogashira" coupling of **13** with benzoyl chloride,^[22] using a procedure previously implemented with an arylated triyne ($R^2 = 4$ -"Pent-C₆H₄ in Scheme 1),^[23] giving **23** with 54 % yield (Scheme 3). The structure of *meso*-**23** was confirmed by XRD analysis of single crystals, spontaneously resolved from a solution of the diastereoisomeric mixture (Figure S.3.1 in Supporting Information).^[21,24]

The Pd-catalytic method did not allow access to the di-*tert*butyl diketone **24** from **13** and pivaloyl chloride. Instead, addition of the dilithium salt of **13** to two equivalents of pivalaldehyde gave the diol **25**, which, after oxidation with MnO_2 , led to **24** with 45 % yield from **13** over two steps.

From the triyne **14** and pivaloyl chloride, however, the pseudo-Sonogashira procedure allowed access to the di-*tert*-butyl diketone **26**, required for the synthesis of **7**. The failure of the Pdcatalytic method for the preparation of **24** can thus be ascribed to the mutual hindrance of the *tert*-butyl groups in both **13** and pivaloyl chloride (Scheme 3).

3. Synthesis of the pericyclynediols 9-12 and carbo-benzenes 5-8

The [6]pericyclynediol **27** (Scheme 4) was first envisaged as a precursor of the [6]pericyclynedione **28**, tetra-*tert*-butyl analogue of **29**, widely used for the synthesis of tetraphenyl-*carbo*benzenes of type **3** (Figure 1).^[1b,10,11,13,18] However, treatment of **21** with the bromomagnesium salt of **13** did not give any trace of **27**, letting the triyne unreacted while giving the diol **22**, likely resulting from Mg-mediated reduction of **21**. Deprotonation of **13** with *n*-BuLi was also attempted, but only trace amounts of **27** and monoadduct **30** could be detected. At last, trans-metallation of the dilithium salt of **13** with CeCl₃ prior to the addition of **21** allowed isolation of **27** with a very low 1 % yield. Here again, the dramatic effect of the replacement of phenyl groups by *tert*-butyl groups is imputable to their mutual hindrance in **13** and **21**.



Scheme 3. Synthesis of C₁₀ dialdehyde and diketones from the triyne 13 or 14.

The synthesis of the [6]pericyclynediols **9-12** was then envisaged by [8+10] macrocyclization of the diketones **23**, **24** and **26** with either the triynes **13** or **14** (Schemes 1, 3, 5). The target products were thus obtained in 14-36 % yield by mixing the reactants in the presence of LiHMDS.

FULL PAPER



Scheme 4. Outcome of reactions of the C₈ trivne 13 with the C₁₀ dialdehyde 21, while targeting the [6] pericyclynediol 27 (nd = yield not determined)

Reduction of 9-12 with SnCl₂/HCl in DCM at room temperature (r.t.) afforded the corresponding carbo-benzenes 5-8, decorated with two to six tert-butyl groups (Scheme 5). Each reaction was monitored by thin layer chromatography (TLC), showing both the disappearance of the starting pericyclynediol spot and the appearance of a strongly coloured spot. While the formation of 6-8 was found to be completed after ca 15 minutes, significant production of hexa-tert-butyl-carbo-benzene 5 required stirring overnight at r. t. The yield was also smaller for 5 (30 %) than for 6 (54 %), 8 (56 %) and 7 (quantitative). While 6, 7 and 8 were isolated as dark red or violet-greenish solids, the hexa-tert-butyl target 5 was found to be a yellow solid. ^tBu groups having no intrinsic chromophoric properties, this unique colour within the series can thus be directly imputed to the C18 ring itself (see section 5). The tert-butyl substituent also have a dramatic effect on both the solubility (s) and stability. As a qualitative comparison, at least 30 mg of 5-8 could be dissolved in 1 mL of DCM or chloroform, while less than 5 mg of 3 or 4 could be (e.g. s = 0.3mg/mL for **3b** in chloroform).^[9]

Di-*tert*-butyl-tetraphenyl-*carbo*-benzene **8** was found to decompose at 280 $^{\circ}$ C,^[9] so at a significantly higher temperature than other tetraphenyl congeners, **3** or **4**. The counterparts **5-7** bearing four or six ^{*t*}Bu groups, were found to be stable beyond 300 $^{\circ}$ C.



Scheme 5. Synthesis of the *carbo*-benzenes 5-8 by [8+10] macrocyclization of the triynes 13 or 14 with the diketones 23, 24 and 26, followed by reductive aromatization of the resulting [6]pericyclynediols 9-12.

10.1002/chem.201800835

WILEY-VCH

FULL PAPER

The ¹H NMR spectrum of **6-8** in CDCl₃ solution exhibits classical features of other phenyl-substituted *carbo*-benzenes, namely a strong deshielding of the *ortho*-¹H nuclei at 9.5-9.6 ppm due to the diatropic ring current over the C₁₈ macrocycle.^[1b,4,8,13,25] The ^tBu ¹H nuclei of **5-8** also resonate at relatively low field (*ca* 2.5 ppm; Figure 2),^[11] with chemical shifts deshielded by 1 ppm as compared to 1,2,3,4- and 2,3,4-5-tetra-*tert*-butylbenzene (1.27-1.49 ppm).^[26] Notably, the hexa-*tert*-butylbenzene, parent of **5**, has been studied at the theoretical level only.^[27] The magnetic aromaticity of **5-8** has been scrutinized in more detail by NICS calculation (see section 7).



Figure 2. ¹H NMR spectra of the tert-butylated carbo-benzenes 5-8 (CDCl₃).

4. X-Ray crystallography of 5-8

The tert-butylated carbo-benzenes 5-8 were characterized by XRD analysis of single crystals deposited from DCM or chloroform solutions (Figure 3, Table 1).^[21,28] A weak diffracting power of crystals of 8 prevented high-quality resolution (R = 10 %), but was sufficient for structural confirmation. The previously reported crystal structure of 4 is here considered as a reference.^[9] In the crystals of 4-7, the asymmetric unit contains a single molecule (two molecules in the crystal of 8), with a quite regular hexagonal C_{18} core, and classical bond lengths and angles (spC-spC \approx 1.22-1.23 Å, and sp^2C - $spC \approx$ 1.37-1.38 Å). The maximum deviation from C_{18} planarity, Δ_1 , is found minimal for 5 (0.037 Å): in spite of the steric crowding due to the six ^tBu groups in 5, these substituents induce three times less distortion than the six phenyl groups in 4 (Δ_1 = 0.11 Å). The same trend is found after DFToptimization of the geometry of **4** and **5** in the gas phase (Δ_1 = 0.007 vs 0.060 Å; see section 7 and Supporting Information).



Figure 3. Molecular views of the X-ray crystal structures of 5-8. Numbering of the non-equivalent C atoms indicative of the crystal symmetry. For clarity, hydrogen atoms, disordered atoms, and solvent molecules are omitted.

The macrocycle of **6** is also almost planar with $\Delta_1 = 0.077(1)$ Å in the crystal (even strictly vanishing in the theoretical gas phase), while those of the less symmetrical counterparts 7 and 8 (ideally C_{2v} , instead of D_{2h} for **6**, C_{6h} or C_{6v} or D_{3d} for **5**) are at least twice more distorted with $\Delta_1 = 0.152(2)$ Å for **7**, 0.282(5) Å for **8**. As far as structural aromaticity is inversely related to geometrical distortion, complementary to Δ_1 , another indicator thereof is the maximum difference of diagonal distances (ca 8.0 ± 0.2 Å in generic *carbo*-benzenes), Δ_2 , which is found three times larger for 4 than for 5, both in the crystal state (0.38 vs 0.12 Å) and in the DFT-theoretical gas phase (0.163 vs 0.054 Å, see section 7: albeit limited, discrepancies in absolute or relative values between experimental and computational data can be ascribed to crystal packing effects). Over the C₁₈^tBu_mPh_{6-m} series, the mean index $(\Delta_1 + \Delta_2)/2$ may formally support a variation of structural aromaticity as 4 < 8 < 7, 6 < 5, i. e. with increasing number m of ^tBu substituents, and decreasing number of Ph substituents. The structural effect of ^tBu groups on the *carbo*-benzene ring is thus opposite to that exerted at the meso positions on the porphyrin core, P2 being reported to be highly distorted.^[29]

The angles θ_i between the mean plane of the C₁₈ ring and those of the phenyl substituents were not found to increase upon increasing the number of ¹Bu substituents, the largest value being 30.8° for the three mixed ¹Bu/Ph representatives **6-8**, close to the 29.9° measured for hexaphenyl-*carbo*-benzene **4**. θ_i values of the same order of magnitude are obtained from DFT optimization in the gas phase (see below). The π -conjugation of the central C₁₈ ring with phenyl substituents is thus not significantly affected in the partially *t*-butylated *carbo*-benzenes **6-8**.

In the crystals of **4-7**, the C₁₈ rings pack in a fully eclipsed manner (without intercalation of any other molecular fragment) in parallel columns along the *b* direction, with quasi-regular hexagonal C₁₈ sections slanted vs the column axis in four ways for **4** (of relative angles $rsa = 18.2^{\circ}$, 65.9, 68.8°) or in two ways for **5** ($rsa = 47.1^{\circ}$), **6** ($rsa = 69.6^{\circ}$) and **7** ($rsa = 49.6^{\circ}$). The two molecules in the asymmetric unit of **8**, belong to parallel columns (along the *c* direction), the C₁₈ sections of which are just slightly slanted vs each other ($rsa = 7.8^{\circ}$).

Except in the crystal of **5**, the shortest C-C distance between C_{18} rings, in the range 3.5 ± 0.1 Å, corresponds to a C-C van der Waals contact: looser than the previously observed attractive π - π stacking in the crystal of **3b** (3.23 Å, Figure 1),^[11b] but quite short considering the ^tBu bulkiness. Truly columnar arrangements are found in crystals of **6** and **7**, where the projections of two closest parallel C₁₈ hexagons along their common normal line (taken as "vertical") on one of their mean planes intersect over *ca* one third of the C₁₈ hexagon surface area, with a columnar deviation from verticality (vs the *b* axis) $\phi = 55.2^{\circ}$ and 59.7° , respectively, close to the one reported for **3b** ($\phi = 55.0^{\circ}$).^[11b] Notably, in all the crystals where applicable, a H atom of a ^tBu substituent points towards the center of a nearest C₁₈ ring, either within a column (as for **6**) (Figure 4) or between neighbouring columns (as for **7**).

Table 1. Selected crystallographic data for 5-8 and 4 (see Figure 4).							
Species	4•CHCl ₃	5	6	7	8•CHCl ₃		
Space group	P2 ₁ 2 ₁ 2 ₁	P21/c	P21/c	<i>C</i> 2/c	<i>P</i> 2 ₁ /n		
no of mean plane	2 X 2	2	2	2	2		
orientations and	18.24°	47.09(2)°	69.58(4)	° 49.70(1)	7.76°		
angles α between	65.88°			۰			
them	68.80°						
Δ_1 = deviation from	0. 11	0.037(2)	0.077(1)	0.152(2)	0.244(5) ^[b]		
C ₁₈ planarity (Å) ^[a]	[0.060]	[0.007]	[0.000]	[0.030]	[0.101]		
Δ_2 = largest diagonal	0.38	0.12	0.11	0.13	0.17 ^[b]		
difference (Å) ^[a]	[0.163]	[0.054]	[0.120]	[0.036]	[0.117]		
Distance d ₁	2.55	4.29	3.52	3.52	(n. a.)		
between fully							
eclipsed ^[c] C ₁₈ ring							
mean planes (Å)							
Shortest C-C	3.55	5.65	3.58	3.45	3.60		
distance d_2 between							
C ₁₈ rings (Å)							
Φ = columnar	82.0°	66.5°	55.2°	59.7°	-		
verticality deviation							
Shortest distance d_3	[d]	1.396	1.536	1.237	0.887		
between a ^t Bu H		(1.574)	(1.739)	(1.458)	(1.202)		
atom and a C ₁₈							
mean plane							
(centroid) (Å)							
Angles θ_i between	2.9-29.9°	-	12.8°	5.5-21.2°	12.9- 30.8		
the C ₁₈ and Ph mean	[0.1-22.5°]	[-]	[0.0°]	[16.2-17.0°]	[0.8-24.1°]		
planes [saled 1 ^[a]							

[a] In square brackets, value calculated in the theoretical gas phase (see section 7). [b] Mean differences for the two non-equivalent molecules of 8: (0.205(4) + 0.282(5))/2 = 0.244(5) Å; (0.18 + 0.15)/2 = 0.16 Å. [c] Eclipse along the *b* direction for **4-7**, not applicable for 8. [d] A distance of 1.31 Å is measured between a Cl atom of the chloroform solvate molecule and both the closest C₁₈ ring mean plane and centroid thereof.



Figure 4. Illustration of the structural descriptors d_1 , d_2 , d_3 , Δ_1 , Δ_2 , α and Φ defined in Table 1 in the case of the *carbo*-benzene **6**.

5. Absorption and emission spectroscopy of 5-8

The *carbo*-benzenes $C_{18}^{t}Bu_mPh_{6-m}$ (**4-8**) are chromophoric compounds, their solid state color varying with m. While **4** and **8** (m = 0, 2) are dark-red, the diphenyl versions **6** and **7** (m = 4) are orange-red, and the hexa-*tert*-butyl version **5** (m = 6, without any phenyl substituent) is yellow. The yellow color of **5**,

6

unprecedented within the *carbo*-benzene family, is attributed to the sole π -delocalization around the C₁₈ ring in the absence of external π -delocalization. Solutions of **5** in organic solvents are also yellow, the maximum absorption wavelength λ_{max} varying from 374 nm in methanol to 379 nm in chloroform (see Figure 5 and Supporting Information). In contrast, all the *carbo*-benzenes reported to date, bearing at least three aryl or alkynyl substituents, give red or violet solutions.^[1b,2,8-11,13,16]

Replacement of two ^{*t*}Bu groups of **5** by two Ph groups induces a bathochromic shift of 30-35 nm in **6** and **7** ($\lambda_{max} = 408$ and 415 nm). Further ^{*t*}Bu \rightarrow Ph replacement induces a similar shift of *ca* 30-35 nm in **8** ($\lambda_{max} = 447$ nm), consistent with the values reported for the three regio-isomers of the tetraphenyl-*carbo*-benzene C₁₈Ph₄H₂ ($\lambda_{max} = 438-444$ nm),^[10] and *p*-^{*i*}Pr₂-C₁₈Ph₄ ($\lambda_{max} = 446$ nm).^[11a] Ultimate ^{*t*}Bu \rightarrow Ph replacement is accompanied by another 25 nm red-shift in **4** ($\lambda_{max} = 472$ nm).^[8,9]

In the porphyrin series (Figure 1), the distortion induced by replacement of the Ph substituents of **P1** by ¹Bu substituents in **P2** is accompanied by a 20 nm bathochromic shift of the Soret band: from 420 nm for **P1**^[30] to 446 nm for **P2**.^[15a] The puckered conformation adopted by hindered *meso*-substituted porphyrins is indeed known to generally induce such a shift.^[15,31] The optical behavior *vs* Ph \rightarrow ¹Bu replacement is thus opposite in the *carbo*-benzene series, with a 100 nm hypsochromic shift from **4** to **5**: this is explained by the absence of steric crowding around the *sp*²-C vertices of the C₁₈ macrocycle.



Figure 5. Normalized absorption spectra of the *carbo*-benzenes **4-8** in chloroform solutions.

The emission properties of **5-8** in the UV-vis region were measured to be very weak, with quantum yields below 1 %, lifetime below 2 ns, and Stoke shifts above 70 nm (Table 2, calculated data in Supporting Information). This is in line with trends reported for most of the *carbo*-benzenes, even those bearing fluorophoric substituents:^[2] to date, the sole example of significant fluorescence has been reported for a bisindolyl derivative and explained by the exceptionally low molar extinction coefficient of the latter.^[32] The high extinction coefficient of **5-8** (ε = 260 000-400 000 L.mol⁻¹.cm⁻¹) and their extremely low fluorescence are in accordance therewith. It was indeed proposed that the very weak fluorescence of *carbo*-benzenes is due to their

very high ε values, any emitted photon being instantly reabsorbed in moleculo.^[32]

Table 2. Emission properties of the carbo-benzenes 5-8 in chloroform solutions. No λ_{absmax} [calcd] ^[a] $10^{-3} \varepsilon$ $\lambda_{em}^{[c]}$ Φ Life-time (nm) [calcd] ^[b] (nm) [calcdf] ^[b] (nm) [calcdf] ^[b] (ns) $4^{8.9}$ 472 $363^{8b}/234^9$ - - - - 5 379 266 446, 485, 505, 530 0.03 1.9 1.9 $[387, 386]$ [2.0, 2.0] [420, 421] [2.4, 2.4] - - - 6 408 411 530, 580 - - - - $[422, 425]$ [1.8, 2.0] [428, 431] [1.8, 2.0] - - - 7 415 407 520, 580 0.1 0.1 - [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4									
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Table 2. Emission properties of the carbo-benzenes 5-8 in chloroform solutions.								
[calcd] ^[a] (L.mol ⁻¹ .cm ⁻¹) [calcd] ^[b] (%) time (ns) 4 ^{8,9} 472 363 ^{8b} /234 ⁹ - - - - [509, 511] [2.3, 2.1] [570, 571] [2.6, 2.5] - - - 5 379 266 446, 485, 505, 530 0.03 1.9 [387, 386] [2.0, 2.0] [420, 421] [2.4, 2.4] - 6 408 411 530, 580 - - [422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] - 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4	No	Io λ_{absmax} $10^{-3} \varepsilon$		$\lambda_{em}^{[c]}$	Φ	Life-			
(nm) [calcd f] ^[b] (nm) [calcd f] ^[b] (ns) 4 ^{8,9} 472 363 ^{8b} /234 ⁹ - -		[calcd] ^[a]	(L.mol ⁻¹ .cm ⁻¹)	[calcd] ^[a]	(%)	time			
4 ^{8,9} 472 363 ^{8b} /234 ⁹ - -		(nm)	[calcd f] ^[b]	(nm)	[calcd f] ^[b]	(ns)			
[509, 511] [2.3, 2.1] [570, 571] [2.6, 2.5] 5 379 266 446, 485, 505, 530 0.03 1.9 [387, 386] [2.0, 2.0] [420, 421] [2.4, 2.4] 6 408 411 530, 580 - ^[d] - ^[d] [422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] - ^[d] 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 8 447 347 520, 550 0.1 0.4	4 ^{8,9}	472	363 ^{8b} /234 ⁹	-	-	-			
5 379 266 446, 485, 505, 530 0.03 1.9 [387, 386] [2.0, 2.0] [420, 421] [2.4, 2.4] 6 408 411 530, 580 - ^[d] - ^[d] [422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] - ^[d] 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 0.4 8 447 347 520, 550 0.1 0.4		[509, 511]	[2.3, 2.1]	[570, 571]	[2.6, 2.5]				
[387, 386] [2.0, 2.0] [420, 421] [2.4, 2.4] 6 408 411 530, 580 - ^[d] - ^[d] [422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] - 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4	5	379	266	446, 485, 505, 530	0.03	1.9			
6 408 411 530, 580 - ^[d] - ^[d] [422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4		[387, 386]	[2.0, 2.0]	[420, 421]	[2.4, 2.4]				
[422, 425] [1.8, 2.0] [428, 431] [1.8, 2.0] 7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4	6	408	411	530, 580	_ [d]	_ [d]			
7 415 407 520, 580 0.1 0.1 [431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4		[422, 425]	[1.8, 2.0]	[428, 431]	[1.8, 2.0]				
[431, 435] [1.5, 2.2] [470, 483] [1.7, 2.6] 8 447 347 520, 550 0.1 0.4	7	415	407	520, 580	0.1	0.1			
8 447 347 520, 550 0.1 0.4		[431, 435]	[1.5, 2.2]	[470, 483]	[1.7, 2.6]				
	8	447	347	520, 550	0.1	0.4			
[476, 478] [1.7, 2.2] [530, 534] [2.0, 2.5]		[476, 478]	[1.7, 2.2]	[530, 534]	[2.0, 2.5]				

[a] See section 7 and Supporting Information. [b] Oscillator strength; see section 7 and Supporting Information. [c] Excitation at $\lambda_{exc} = \lambda_{absmax}$. [d] The fluorescence of **6** was too low to allow accurate determination of the quantum yield and life time.

6. Electrochemistry of 5-8

Electrochemical properties of 5-8 were investigated by squarewave (SW) and cyclic voltammetry (CV) (Table 3). In all cases, three reduction and three oxidation waves were evidenced by SWV. The first reduction of 5-8 was found to be reversible, at a potential increasing with the number of phenyl substituents, consistently with the overall π -conjugation extent: -1.36 V for hexa-*tert*-butyl-carbo-benzene 5, -1.04 ± 0.01 V for the diphenyl counterparts 6 and 7, -0.88 V for the tetraphenyl congener 8, and -0.72 V for the hexaphenyl reference 4.^[9] The second reduction process was also found to be reversible for 6-7 ($-1.50 \pm 0.07 \text{ V}$) and 8 (-1.31 V), but was not for the homoleptic references 5 (-1.75 V) and 4 (-1.15 V).^[9] In oxidation regime, the first process, occurring invariably at 1.13 ± 0.01 V, was found reversible for 5-8 (at high scan rate only for $\mathbf{8}$). In contrast, the oxidized product $\mathbf{4}^+$ was observed to polymerize at the anode $(E_p^{ox} = 1.14 \text{ V})$.^[9] The oxidation reversibility is thus found to increase with the number of ^tBu substituents at the C₁₈ ring, their σ -donor effect being indeed prone to stabilize the oxidized species.

The electrochemical behavior of *meso*-substituted porphyrins follows the same trend: alkyl substituents make the compounds more difficult to reduce and easier to oxidize, at least in a reversible manner.^[33]

Table 3. SWV and CV data for the carbo-benzenes 4-8.								
No	Red	uctions		Oxidations				
	$E_{1/2}^{[a]} (\Delta E_{P})^{[b]}$	$RI_{P}^{[c]}$	E _P ^{red [d]}	$E_{1/2}^{[a]} (\Delta E_P)^{[b]}$	$RI_{P}^{[c]}$	$E_{P}^{ox[d]}$		
4 ⁹	-0.72 (0.44)	0.58	-1.15	-	-	1.14		
5	-1.36 (0.74)	0.96		1.13 (0.68)	0.95			
			-1.75			1.84		
			-2.00			2.13		
6	-1.03 (0.73)	0.89		1.12 (0.63)	1.02			
	-1.43 (0.68)	1.03				1.68 ^[e]		
			-2.03			2.27		
7	-1.05 (0.68)	0.87		1.14 (0.69)	1.04			
			-1.57 ^[e]			1.75		
			-1.84			2.03		
8	-0.88 (0.73)	0.99		-	-	1.18 ^[e]		
	-1.31 (0.73)	0.85				1.72		
			-1.86			2.00		

Measurements performed at r. t. in DCM; supporting electrolyte: [*n*-Bu₄N][PF₆] (0.1 M); working electrode: Pt; reference electrode: saturated calomel electrode (SCE, 0.242 V *vs* the hydrogen electrode); scan rate: 0.2 V.s⁻¹ unless otherwise noted. [a] Half-wave potential $E_{1/2} = (E_P^{red} + E_P^{ox})/2$, in V/SCE. [b] Separation between the two peak potentials: $\Delta E_P = IE_P^{red} - E_P^{ox}|$, in V. [c] Peak current ratio R/_P = I/_P^{ox}/I_P^{red}]. [d] *E*_P values measured from CV in V/SCE. [e] Reversibility observed at high scan rate only (5 V.s⁻¹).

7. DFT computational characterization of 5-8

The geometry of the isolated carbo-benzenes 4-8, C₁₈H₆ and C₁₈F₆ was optimized at the B3PW91/6-31G(d,p) level without symmetry constraint using the Gaussian09 program (Supporting Information).^[34] The calculated bond lengths reproduce crystallographic data within a 0.01 Å difference limit, without significant variation with the substitution pattern (Csp–Csp \approx 1.24 Å, Csp-Csp² ≈ 1.38 Å , C-^tBu≈ 1.54 Å, C-Ph ≈ 1.48 Å). A quasi- D_{6h} symmetry is obtained for the C₁₈ core of **5**, with a negligible deviation from planarity: $\Delta_1 = 0.007$ Å for **5** vs 0.060 Å for **4**, confirming the trend observed in the crystal state (Table 1). As stated in section 4, crystallography and DFT calculations converge for a relative structural aromaticity in the order: 4 < 8 < 7, 6 < 5. Regarding the θ_i angles between the means planes of the C₁₈ core and Ph substituents, differences with experimental values reveal crystal packing effects (Table 2). In the absence of such effects, it is remarkable that $\theta_i = 0^\circ$ for **6** whose two Ph substituents are adjacent to two o-^tBu substituents: the latter thus induce less strain than the former allowing perfect π -conjugation of the C₁₈ core with such "isolated" Ph substituents.

The near-frontier molecular orbitals (i.e. non-strictly degenerated HOMO and HOMO-1 on one hand, LUMO and LUMO+1 on the other hand), though remaining mainly localized on the C₁₈ core operating as a nodal surface (thus of π_z nature), are more sensitive to the substituents in terms of energy (see Supporting Information). As expected, the HOMO-LUMO gap η , i.e. twice the original definition of chemical hardness by Pearson,^[35] is minimal for **4**, exhibiting the largest π -conjugation extent ($\eta = 0.084$ Ha; see Table 4). The gap is consistently much larger for **5** ($\eta = 0.103$ Ha), albeit smaller than for C₁₈H₆ ($\eta = 0.108$ Ha) and C₁₈F₆ ($\eta = 0.106$ Ha). While the HOMOs and LUMOs of phenylated or fluorinated *carbo*-benzenes are partly delocalized over the substituents, those of C₁₈H₆ and **5** are almost exclusively

WILEY-VCH

concentrated over the C₁₈ core, for which the [']Bu groups thus act as π -insulators (Supporting Information).

As also expected from the strong σ -donating character of ^{*t*}Bu substituents, **5** exhibits a maximal chemical potential ($\mu = -0.139$ Ha), i.e. a minimum electronegativity in the Mulliken-Pearson scale,^[35e] and a minimal electrophilicity^[35b] ($\omega = \mu/(2\eta) = 0.094$ Ha) within the series: **5** is thus predicted more stable than **4** ($\omega = 0.135$ Ha) towards all kinds of nucleophiles (in addition to the steric protection brought by the crown of ^{*t*}Bu groups). For comparison, consistently with the high electronegativity of fluorine atoms, C₁₈F₆ exhibits a minimal chemical potential ($\mu = -0.181$ Ha) and a maximal electrophilicity ($\omega = 0.153$ Ha).

TD-DFT calculations of excited states allowed simulation of the absorption spectra. As previously shown for other *carbo*benzenes, ^[1c,2,13] the lowest energy excitations $|S_0> \rightarrow |S_1>$ and $|S_0> \rightarrow S_2>$ take place in the blue-green region with a weak oscillator strength, each of them involving near-frontier oneelectron transitions, $H \rightarrow L \& H-1 \rightarrow L+1$ and $H \rightarrow L+1 \& H-1 \rightarrow L$ (see section 6.4 in the Supporting Information). In accordance with the four-orbital Gouterman model, the same one-electron transitions are involved in the two next excitations $|S_0> \rightarrow |S_3>$ and $|S_0> \rightarrow |S_4>$ underlying the most intense absorption band, shifted from the blue region for **4** to the violet region for **5-8**. These two excitations are close both in energy and oscillator strength and can thus be averaged to calculate λ_{max} values, which happen to fit perfectly with the experimental values (Figure S.6.4., eqn. 1).

 $\lambda_{\max}(\text{exptl.}) \approx 0.745 \ \lambda_{\max}(\text{calcd.}) + 92.2, R > 0.999 \quad (\text{eqn. 1}).$

Table 4.	DFT	calculated	electronic	properties	of	4-8 ,	3c,	$C_{18}H_6$	and	C ₁₈ F
(B3PW9 ⁻	1/6-31	G(d,p) or 6-	-31+G(d,p)	level).						

	Е _{номо} ^{а)} Е _{номо-1}	E _{LUMO} ^{a)} E _{LUMO+1}	$\mu^{b)}$	$\eta^{{ m c})}$	ω^{d}	NICS(0)/ NICS(1) ^{e)}
C ₁₈ H ₆	-0.214	-0.106	-0.160	0.108	0.119	-18.1/-16.5
	-0.214	-0.106				
3c ^[11a]	-0.191	-0.106	-0.151	0.085	0.135	-14.7/-13.4
	-0.197	-0.098				
4	-0.193	-0.109	-0.148	0.084	0.119	-13.5/-12.4
	-0.195	-0.108				
5	-0.190	-0.087	-0.139	0.103	0.094	-17.2/-15.7
	-0.192	-0.085				
6	-0.189	-0.100	-0.144	0.088	0.118	-15.7/-14.3
	-0.196	-0.090				
7	-0.190	-0.098	-0.144	0.093	0.112	-15.9/-14.6
	-0.194	-0.092				
8	-0.192	-0.104	-0.148	0.088	0.124	-14.6/-13.4
	-0.194	-0.101				
$C_{18}F_6$	-0.234	-0.127	-0.181	0.106	0.153	-17.9/-18.9
	-0.234	-0.127				

[a] HOMO and LUMO energies, in Ha.; due to a near D_{6h} symmetry, HOMO and LUMO are quasi-degenerated with HOMO–1 and LUMO+1, respectively (see Supporting Information). [b] Chemical potential, $\mu = (E_{HOMO} + E_{LUMO})/2$, in Ha/e; [c] chemical hardness, $\eta = E_{LUMO} - E_{HOMO}$, in Ha/e². [d] Electrophilicity, $\omega = \mu^2/2\eta$, in Ha. [e] Calculated at the B3PW91/6-31+G(d,p)//6-31G(d,p) level within the GIAO formalism, in ppm.

The variation of local aromaticity of the C_{18} ring has also been appraised for the magnetic criterion. Although accurate data

would rely on current density maps, relevant approximations can be gained from a single numerical index: the nucleus independent chemical shift (NICS), calculated at the B3PW91/6-31+G(d,p) level,^[36] at either the ring center (NICS(0)) or 1 Å above (NICS(1)). A tight correlation between NICS(0) and NICS(1) is found over the series 4-8, $C_{18}H_6$ and p-^{*i*}Pr- $C_{18}Ph_4$ (3c):^[11a] NICS(1) = 0.90 NICS(0) - 0.3 (Table 4 and Supporting Information). Taking the theoretical unsubstituted parent C₁₈H₆ as a reference, the NICS(0) value has been previously observed to decrease whichever substitution takes place.^[11a,13,37] This is confirmed and refined in the present series, showing that the magnetic aromaticity decreasing effect is stronger for aryl substituents than for alkyl counterparts: for homoleptic carbo-benzenes C18R6, the NICS(0)/NICS(1) values indeed increase from -18.1/-16.5 ppm for R = H, to -17.2/-15.7 ppm for R = ^tBu (5) and -13.5/-12.4 ppm for R = Ph (4). The effect is thus *ca* five time stronger for Ph groups than for ^tBu group.

Notably, NICS values of the phenyl substituents are found below –5.4 ppm, *vs* –8.3 ppm for the benzene molecule (see Supporting Information),^[11a,36,37] showing that their magnetic aromatic character is also severely reduced by attachment to the C₁₈ core: the C₆-C₁₈ π-conjugation ($\theta_i < 30^\circ$, Table 2) indeed decreases their local chemical hardness and thus their magnetic aromaticity (see discussion below).

In the tetraphenyl series, *o*- or p-R₂-C₁₈Ph₄, the NICS(0)/NICS(1) values of the C₁₈ core remain almost constant, at -14.6/-13.4 ppm for R = *o*-^tBu (8) and -14.7/-13.4 ppm for R = *p*-^tPr (3c).^[11a] The effects of substitution by 'Bu and F are comparable: NICS(0) = -17.2 and -17.9 ppm, respectively.

NICS(0) is found to decrease vs chemical hardness or HOMO-LUMO gap η , and even more regularly with NICS-effective counterpart η_{eff} (as defined in section 6.6 of the Supporting Information).^[38] More remarkably still, NICS(0) increases with calculated λ_{max} values (or experimental values through the above eqn. 1) through an accurate linear correlation for 3c,^[11a] 4-8, C₁₈H₆ and C₁₈F₆ (Figure 6a and Supporting Information). This correlation, albeit over a limited set of compounds, spans a bridge between the energetic and magnetic criteria of aromaticity:[39a] from a heuristic viewpoint, hard (i.e. poorly polarizable) electronic systems, primarily characterized by large HOMO-LUMO gaps and more generally by low λ_{max} values, should indeed be more prone to resist deviation of a ring current induced by an external magnetic field.^[6] The correlation is empirical in nature, but the practical consideration of λ_{max} instead of λ_1 , the first excitation wavelength with vanishing oscillator strength (see section 6.6 in the Supporting Information), is also intuitively justified by the common dynamical nature of the phenomena underlying NICS and λ_{max} (a large oscillator strength or transition dipole moment features a high absorption probability). Nevertheless, as far as the spectral pattern remains the same, λ_1 also correlates with λ_{max} (Figure S.4.2 in the Supporting Information).

Further, following a scheme proposed by Haley et al. for a series of antiaromatic indenofluorenes,[40] a regular correlation is also found between the first reduction potential E1/2red (Table 3) and NICS(0) (Figure 6b). As very recently disclosed in the carbo-OPE series,^[1e] the expected qualitative correlation between $E_{1/2}^{\text{red}}$ and





Figure 6. a (*top*) Variation of NICS(0) with calculated values of UV-vis absorption wavelengths of highest oscillator strengths (actually arithmetic mean over two very close excited states: see Table 4 and Supporting Information). **b** (*bottom*) Variation of the first reduction potential $E_{1/2}^{\text{red}}$ (Table 3) vs NICS(0) following Haley's scheme.^[40]

Conclusions

The above-described preparation and characterization of *tert*butylated/ phenylated *carbo*-benzenes show that ^tBu groups in *ortho* position do not induce distortion of the C₁₈ ring, and that the presence of at least three aryl substituents is not a requirement for experimental stability. The complete series C₁₈^tBu_mPh_{6-m} exhibits regular variations of key properties *vs* m = 0, 2, 4, 6: increasing solubility, stability and chemical hardness (η) on one hand, decreasing maximum UV-vis absorption wavelength (λ_{max}), reduction potential and NICS on the other hand. In the considered

carbo-benzene series, the correlations of NICS *vs* λ_{max} , η and $E_{1/2}^{\text{red}}$ illustrate that *aromatic* systems are *hard* chemical systems. More practically, as the poor solubility of arylated *carbo*-benzenes hampers their use for applications (e. g. high-quality thin film deposition for organic photovoltaics),^[9] the solubilizing effect of *tert*-butyl substituents opens promising prospects. In particular, the implemented methodology for the synthesis of **6** could be applied for the preparation of soluble versions *p*-R₂-C₁₈^tBu₄ of poorly tractable *p*-R₂-C₁₈Ph₄ leads, while deserving deeper studies of their photo-physical properties.^[2,13,16]

Experimental Section

General

THF, diethyl ether (Et₂O), pentane and dichloromethane (DCM) were dried with a PureSolv-MD-5 Innovative Technology system for the purification of solvents. All other reagents were used as commercially available. In particular, solutions of n-BuLi were 1.6 M or 2.5 M in hexane, solutions of EtMgBr were 3 M in THF, solutions of HCl were 2 M in diethyl ether, solutions of ethynylmagnesium bromide were 0.5 M in THF. All reactions were carried out under argon atmosphere using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 µm). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed under UV-light and/or by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used, ¹H and ¹³C NMR: Avance 400 and Avance 400 HD spectrometers; mass spectroscopy: TSQ 7000 Thermo Electron and Voyager DE-ST Perseptive Biosystems spectrometers; UV-Visible: Perkin-Elmer UV-Vis Win-Lab Lambda 35; IR: Perkin Elmer 1725. NMR chemical shifts are given in ppm with positive values to high frequency relative to the tetramethylsilane reference. Coupling constants J are in Hertz. UV-Visible extinction molar coefficient ε is in L^{-mol⁻¹} cm⁻¹ and wavelengths λ in nm.

Voltammetry

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 controled by GPES 4.09 software. Experiments were performed at room temperature in a home-made airtight three-electrode cell connected to a vacuum/agon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1 cm² apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [n-Bu₄N][PF₆] was used as received (Fluka, 99 % electrochemical grade) and simply degassed under argon. The solutions used in the electrochemical study was 10⁻³ M in carbobenzene and 0.1 M in supporting electrolyte. Before each measurement, the solutions are degassed by bubbling argon, and the working electrode was polished with a polishing machine (Presi P230). Typical instrumental parameters for recording square-wave voltammograms were: SW frequency f = 20 Hz, SW amplitude Esw = 20 mV, scan increment dE = 0.5 mV.

Crystallography

Excepted for the hexa-tertbutyl-*carbo*-benzene **5**, intensity data were collected at low temperature on an Apex2 Bruker diffractometer equipped with a 30W air-cooled microfocus source ($\lambda = 0.71073$ Å) or on a Gemini Oxford Diffraction diffractometer ($\lambda = 0.71073$ Å). Data collection for **5** was performed on a high flux microfocus Rigaku FRX rotating anode at the

WILEY-VCH

copper K_a wavelength equipped with a Dectris Pilatus 200K hybrid detector. The structures were solved using SUPERFLIP, and refined by means of least-squares procedures on F using the programs of the PC version of CRYSTALS.^[41] Atomic scattering factors were taken from the international tables for X-ray crystallography.^[42] The asymmetric unit consists in a whole molecule (with or without solvent), except for **8** (2 molecules per asymmetric unit) and for **6**, **13** and **23** (half a molecule per asymmetric unit). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN. For **5**, **7**, **8** and **18**, several disorders were modelled with respect to the electronic densities. Moreover, crystals of **5** were found to be inherently twinned.

Computational methods

All the DFT static calculations have been performed at the GGA level with the Gaussian09 set of programs,^[34] using the B3PW91 functional of Becke, Perdew and Wang.^[43] The electronic configuration of the molecular systems was described with the 6-31G(d,p) basis set for H, C, and O (6-31G** keyword in Gaussian) for the geometry optimizations.^[44] The geometry optimizations were carried out without symmetry constraints, and the characterization of the stationary points was performed by analytical frequency calculations. Using the equilibrium geometries, calculations of electronic spectra (absorption and emission) and NICS were performed at the TDDFT level with the 6-31+G(d,p) basis set, within the framework of the GIAO formalism.^[45] Data were treated with ROTAX which gave the twin law between the two components (0.94: 0.06). Refinement of the final models led to imperfect but reasonable solutions. The same data were obtained after running single point energy calculations with the program Firefly v. 8.1.1 from the geometries optimized using Gaussian09.^[46] Molecular orbitals were edited using the interface program MacMolPlt, v. 7.7.[47]

Acknowledgements

The authors thank the Toulouse IDEX Emergence program 2014 (*Carbo*-device project) for the post-doctoral grant of D. L. and for funding. R. C. thanks the Centre National de la Recherche Scientifique (CNRS) for half a teaching sabbatical in 2015-2016. In the framework of the CNRS RÉCIPROCS network, this work has benefited from the X-ray facility of the Biophysical and Structural Chemistry platform at IECB, CNRS UMS 3033, INSERM US 001, Bordeaux University. Dr. Brice Kauffmann is particularly acknowledged for the DRX analysis of compound **5**.

Keywords: aromaticity • *carbo*-benzene • electronic insulation • substituent effect • *tert*-butyl group

- a) For a recent review, see: J. L. Marshall, D. Lehnherr, B. D. Linder, R. R. Tykwinski, *ChemPlusChem* 2017, *82*, 967-1001; b) K. Cocq, C. Lepetit, V. Maraval, R. Chauvin, *Chem. Soc. Rev.* 2015, *44*, 6535-6559, and references therein; c) most recent article on *carbo*-benzenes: C. Zhu, A. Poater, C. Duhayon, B. Kauffmann, A. Saquet, R. Chauvin, *Angew. Chem. Int. Ed.* 2018, *in press.* DOI: 10.1002/anie.201713411.
- [2] See for example: I. Baglai, M. de Anda-Villa, R. M. Barba-Barba, C. Poidevin, G. Ramos-Ortíz, V. Maraval, C. Lepetit, N. Saffon-Merceron, J.-L. Maldonado, R. Chauvin, *Chem. Eur. J.* 2015, *21*, 14186-14195.
- [3] Z. Li, M. Smeu, A. Rives, V. Maraval, R. Chauvin, M. A. Ratner, E. Borquet, *Nat. Commun.* 2015, 6:6321.

FULL PAPER

- [4] See for example: C. Poidevin, J.-P. Malrieu, G. Trinquier, C. Lepetit, F. Allouti, M. E. Alikhani, R. Chauvin, *Chem. Eur. J.* 2016, 22, 1-15.
- [5] C. Zhu, T.-H. Wang, C.-J. Su, S.-L. Lee, A. Rives, C. Duhayon, B. Kauffmann, V. Maraval, C.-h. Chen, H.-F. Hsu, R. Chauvin, *Chem. Commun.* **2017**, 53, 5902-5905.
- [6] R. Chauvin, C. Lepetit, V. Maraval, L. Leroyer, *Pure Appl. Chem.* 2010, 82, 769-800.
- [7] C. Zou, C. Duhayon, V. Maraval, R. Chauvin, Angew. Chem. Int. Ed. 2007, 46, 4337-4341.
- [8] a) Y. Kuwatani, N. Watanabe, I. Ueda, *Tetrahedron Lett.* **1995**, *46*, 119-122; b) R. Suzuki, H. Tsukuda, N. Watanabe, Y. Kuwatani, I. Ueda, *Tetrahedron* **1998**, *54*, 2477-2496.
- C. Zhu, C. Duhayon, D. Romero-Borja, J.-L. Maldonado, G. Ramos-Ortíz, A. Saquet, V. Maraval, R. Chauvin, *New. J. Chem.* 2017, *41*, 3908-3914, and references therein.
- [10] K. Cocq, V. Maraval, N. Saffon-Merceron, R. Chauvin, Chem. Rec. 2015, 15, 347-361.
- [11] a) K. Cocq, N. Saffon-Merceron, A. Poater, V. Maraval, R. Chauvin, *Synlett* **2016**, *27*, 2105-2112; b) C. Zhu, A. Rives, C. Duhayon, V. Maraval, R. Chauvin, *J. Org. Chem.* **2017**, *82*, 925-935.
- [12] R. Chauvin, Tetrahedron Lett. 1995, 36, 401-404.
- [13] L. Leroyer, C. Lepetit, A. Rives, V. Maraval, N. Saffon-Merceron, D. Kandaskalov, D. Kieffer, R. Chauvin, *Chem. Eur. J.* 2012, *18*, 3226-3240.
- [14] a) M. Gouterman, J. Chem. Phys. 1959, 30, 1139-1161; b) M. Gouterman, J. Mol. Spectrosc. 1961, 6, 138-163; c) P. J. Spellane, M. Gouterman, A. Antipas, S. Kim, Y. C. Liu, Inorg. Chem. 1980, 19, 386-391.
- [15] a) M. O. Senge, I. Bischoff, N. Y. Nelson, K. M. Smith, J. Porphyrins Phthalocyanines 1999, 3, 99-116; b) A. B. Ormond, H. S. Freeman, Dyes and Pigments 2013, 96, 440-448.
- [16] A. Rives, I. Baglai, V. Malytskyi, V. Maraval, N. Saffon-Merceron, Z. Voitenko, R. Chauvin, *Chem. Commun.* 2012, 48, 8763-8765.
- [17] For early references on pericyclynes see: a) L. T. Scott, G. J. DeCicco, J. L. Hyun, G. Reinhardt, J. Am. Chem. Soc. 1983, 105, 7760-7761; b) L. T. Scott, G. J. DeCicco, J. L. Hyun, G. Reinhardt, J. Am. Chem. Soc. 1985, 107, 6546-6555. For an early reference on hexaoxy[6]pericyclynes, see: c) C. Saccavini, C. Tedeschi, L. Maurette, C. Sui-Seng, C. Zou, M. Soleilhavoup, L. Vendier, R. Chauvin, Chem. Eur. J. 2007, 13, 4895-4913.
- [18] L. Leroyer, C. Zou, V. Maraval, R. Chauvin, C. R. Chimie 2009, 12, 412-429.
- [19] For the synthesis of 15 by AlCl₃-promoted acylation, see: O. Klein, H. Hopf, J. Grunenberg, *Eur. J. Org. Chem.* 2009, 2141-2148.
- [20] For the characterization of **15**, see: a) L. Birkofer, K. Richtzenhain, *Chem. Ber.* **1979**, *112*, 2829-2836; b) S. Eagon, C. Delieto, W. J. McDonald, D. Haddenham, J. Saavedra, B. Singaram, *J. Org. Chem.* **2010**, *75*, 7717-7725.
- [21] CCDC 1523150-1523156 (18, 13, 7, 5, 6, 8, 16) and CCDC 1525999 (23) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures. a) Crystallographic data for **16**: $C_{12}H_{20}OSi$, *M* = 208.38, monoclinic, space group $P2_1/n$, a = 14.2363(3) Å, b = 6.51895(12) Å, c = 14.4834(3) Å, $\alpha =$ 90°, β = 95.7989(18)°, γ = 90°, V = 1337.27(3) Å³, Z = 4, T = 120 K, 39847 collected reflexions, 4560 unique reflexions (R_{int} = 0.029), $R[I>3\sigma(I)]$ = 0.030 for 3852 contributing reflexions; b) crystallographic data for 18: C₂₃H₄₀O₂Si₂, *M* = 404.74, triclinic, space group *P*-1, *a* = 11.1519(4) Å, *b* = 11.1745(5) Å, c = 11.2463(4) Å, α = 92.786(2)°, β = 110.218(2)°, γ = 96.628(2)°, V = 1300.44(5) Å³, Z = 2, T = 100 K, 70763 collected reflexions, 7830 unique reflexions (R_{int} = 0.036), $R[I>3\sigma(I)]$ = 0.057 for 5605 contributing reflexions; c) crystallographic data for 13: C₁₈H₂₆O₂, M = 274.40, monoclinic, space group P21/c, a = 7.4651(8) Å, b = 6.2827(6) Å, c = 18.2015(17) Å, $\alpha = 90^{\circ}$, $\beta = 99.828(3)^{\circ}$, $\gamma = 90^{\circ}$, V = 841.14(8) Å³, Z = 2, T = 100 K, 16601 collected reflexions, 2349 unique reflexions (R_{int} = 0.036), $R[I>3\sigma(I)] = 0.101$ for 1867 contributing reflexions.

- [22] R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant, A. Kantacha, *Chem. Commun.* **2005**, 1037-1039.
- [23] K. Cocq, N. Saffon-Merceron, Y. Coppel, C. Poidevin, V. Maraval, R. Chauvin, Angew. Chem. Int. Ed. 2016, 55, 15133-15136.
- [24] Crystallographic data for **23**: C₃₂H₃₄O₄, *M* = 482.62, monoclinic, space group *P*2₁/c, *a* = 6.1720(3) Å, *b* = 19.9189(9) Å, *c* = 10.8454(5) Å, *α* = 90°, *β* = 92.902(3)°, *γ* = 90°, *V* = 1331.62(6) Å³, *Z* = 2, *T* = 100 K, 18919 collected reflexions, 3318 unique reflexions (*R*_{int}= 0.064), *R*[*I*>3*σ*(*I*)] = 0.101 for 2575 contributing reflexions.
- [25] A. Soncini, P. W. Fowler, C. Lepetit, R. Chauvin, Phys. Chem. Chem. Phys. 2008, 10, 957-964.
- [26] A. Krebs, E. Franken, S. Müller, *Tetrahedron Lett.* **1981**, *22*, 1675-1678.
 [27] a) J. Zhang, D. M. Ho, R. A. Pascal Jr, *J. Am. Chem. Soc.* **2001**, *123*, 10919-10926; b) D. Nori-Shargh, D. Tahmassebi, M. Poukalhor, M. M. Amini, S. Jameh-Bozorghi, F. Deyhimi, M. Khanizadeh, M.
- Malekhosseini, Phosphorus, Sulfur, and Silicon 2006, 181, 2419-2434. a) Crystallographic data for 5: C₄₂H₅₄, M = 598.87, monoclinic, space [28] group $P2_1/c$, a = 11.9018(3) Å, b = 10.7319(3) Å, c = 29.1858(7) Å, $\alpha = 10.7319(3)$ Å, c = 29.1858(7) Å, $\alpha = 10.7319(3)$ 90°, β = 101.639(2)°, γ = 90°, V = 3654.23(9) Å³, Z = 4, T = 120 K, 24805 collected reflexions, 7164 unique reflexions ($R_{int} = 0.020$), $R[I>3\sigma(I)] =$ 0.077 for 6193 contributing reflexions; b) crystallographic data for 6: C₄₆H₄₆, *M* = 598.87, monoclinic, space group *P*2₁/c, *a* = 14.8944(12) Å, b = 6.1633(5) Å, c = 19.8087(16) Å, $\alpha = 90^{\circ}$, $\beta = 98.675(3)^{\circ}$, $\gamma = 90^{\circ}$, $V = 10^{\circ}$ 1797.61(15) Å³, Z = 2, T = 100 K, 43406 collected reflexions, 5873 unique reflexions (R_{int} = 0.059), $R[I>3\sigma(I)]$ = 0.043 for 3782 contributing reflexions; c) crystallographic data for 7: C₄₆H₄₆, *M* = 598.87, monoclinic, space group C2/c, a = 32.232(2) Å, b = 10.6973(7) Å, c = 23.3273(14) Å, $\alpha = 90^{\circ}, \beta = 114.6906(16)^{\circ}, \gamma = 90^{\circ}, V = 7307.8(4) \text{ Å}^3, Z = 8, T = 100 \text{ K},$ 95255 collected reflexions, 12797 unique reflexions (R_{int}= 0.033), $R[I>3\sigma(I)] = 0.059$ for 10529 contributing reflexions; d) crystallographic data for 8: C_{50.50}H_{38.50}Cl_{1.50}, *M* = 698.54, monoclinic, space group *P*2₁/n, a = 9.6382(5) Å, b = 16.4828(9) Å, c = 48.783(2) Å, $\alpha = 90^{\circ}$, $\beta =$ 93.921(3)°, γ = 90°, V = 7731.8(4) Å³, Z = 8, T = 100 K, 51106 collected reflexions, 12872 unique reflexions (R_{int} = 0.056), $R[I>2.7\sigma(I)]$ = 0.101 for 9535 contributing reflexions.
- [29] For the synthesis of the 5,10,15,20-tetra-tert-butyl-porphyrin see: a) T. Ema, M. O. Senge, N. Y. Nelson, H. Ogoshi, K. M. Smith, Angew. Chem. Int. Ed. 1994, 33, 1879-1881. For the XRD structure see: b) M. S. Somma, C. J. Medforth, N. Y. Nelson, M. M. Olmstead, R. G. Khoury, K. M. Smith, Chem. Commun. 1999, 121-1222.
- [30] K. M. Smith, Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975.
- [31] C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks, J. A. Shelnutt, J. Am. Chem. Soc. 1992, 114, 9859-9869.
- [32] I. Baglai, V. Maraval, Z. Voitenko, Y. Volovenko, R. Chauvin, French-Ukrainian J. Chem. 2013, 1, 48-53.
- [33] C. Paliteiro, A Sobral, *Electrochemica Acta* 2005, 50, 2445-2541.
- Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, [34] G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox,. Gaussian, Inc., Wallingford CT, 2009.
- [35] a) R. G. Pearson, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 8440-8441; b) P.
 K. Chattaraj, S. Giri, S. Duley, *J. Chem. Phys. Lett.* **2010**, *1*, 1064-1067;
 c) R. G. Pearson, Chemical Hardness: Applications from Molecules to

FULL PAPER

Solids; Wiley-VCH: New York, 1997; d) A. Poater, A. Gallegos, R. Carbó-Dorca, J. Poater, M. Solà, L. Cavallo, A. P. Worth, *J. Comput. Chem.* **2009**, *30*, 275-284; e) R. G. Pearson, *Inorg. Chem.* **1988**, *27*, 734-740.

- [36] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, J. R. V. Hommes, J. Am. Chem. Soc. 1996, 118, 6317-6318.
- [37] C. Godard, C. Lepetit, R. Chauvin, *Chem. Commun.* **2000**, 1833-1834.
- In the absence of strict D_{6h} symmetry, the active frontier MOs are not [38] strictly pairwise degenerated (HOMO ≠ HOMO-1, LUMO ≠ LUMO+1): near to degeneracy, a relevant Pearson's hardness should thus involve all of them four. Effective HOMO and LUMO energies can thus be defined as E_{HOMOeff} = w E_{HOMO-1} + (1-w) E_{HOMO} and E_{LUMOeff} = w' E_{LUMO+1} + $(1-w') E_{LUMO}$, where the weighting coefficients w, w' must be equal to unity for perfect degeneracy, and vanish as drawing farther from it. Taking the simplest form $w = k/(k + E_{HOMO} - E_{HOMO-1})$ and $w' = k/(k + E_{LUMO+1} - E_{LUMO})$, and defining the effective hardness as $\eta_{\text{eff}} = E_{\text{LUMOeff}} - E_{\text{HOMOeff}}$, a perfect linear correlation is obtained for k = 0.0072: NICS(0) = 5.0 - 214 η_{eff} with a reliability coefficient R > 0.9999 over a set of seven compounds: 4, 6, 7, 8, p- ${}^{i}Pr_{2}C_{18}Ph_{4}$, $C_{18}H_{6}$ and $C_{18}F_{6}$. The NICS(0) value predicted for 5 by this equation (with η_{eff} = 0.106 Ha) is –17.7 ppm, instead of –17.2 ppm calculated (a perfect fit would be obtained for the value η_{eff} = 0.104 Ha). See Supporting Information.
- [39] For a seminal paper about the aromaticity issue, see: M. K. Cyranski, T. Krygowski, A. R. Katritzky, P. v. R. Schleyer, J. Org. Chem. 2002, 67, 1333-1338, and citations therein.

- [40] C. K. Frederickson, L. N. Zakharov, M. M. Haley, J. Am. Chem. Soc. 2016,138, 16827-16838.
- [41] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, J. Appl. Cryst. 2003, 36, 1487.
- [42] International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, England, **1974**.
- [43] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652; b) J. P. Perdew, Y. Wang, Phys. Rev. B 1992, 45, 13244-13249.
- [44] a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724;
 b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294-301.
- [45] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, J. R. V. Hommes, J. Am. Chem. Soc. 1996, 118, 6317-6318.
- [46] a) A. A. Granovsky, *Firefly version 8,* <u>http://classic.chem.msu.su:gran:firefly:index.html</u>) which is partially based on the GAMESS (US) source code; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347-1363.
- [47] B. M. Bode, M. S. J. Gordon, J. Mol. Graph. Model. 1998, 16, 133-138.

FULL PAPER

Entry for the Table of Contents

FULL PAPER

A crown of six *tert*-butyl groups acts as a steric bumper and π -electronic insulator of the *carbo*-benzene ring, unveiling intrinsic features of the C₁₈ aromatic core.



D. Listunov, C. Duhayon, A. Poater, S. Mazères, A. Saquet, V. Maraval,* R. Chauvin*

Page No. – Page No. Steric/π-electronic insulation of the *carbo*-benzene ring: dramatic effects of *tert*-butyl vs phenyl crowns on geometric, chromophoric, redox and magnetic properties