# Chromophores

# Functional *carbo*-Butadienes: Nonaromatic Conjugation Effects through a 14-Carbon, 24- $\pi$ -Electron Backbone

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**Abstract:** A systematic study of *carbo*-butadiene motifs not embedded in an aromatic *carbo*-benzene ring is described. Dibutatrienylacetylene (DBA) targets R<sup>1</sup>–C(R)=C=C=C(Ph)–  $C=C-C(Ph)=C=C=C(R)-R^2$  are devised, in which R is  $C=CSiiPr_3$  and R<sup>1</sup> and R<sup>2</sup> are R, H, or 4-X-C<sub>6</sub>H<sub>4</sub>, with the latter including three known representatives (X: H, NMe<sub>2</sub>, or NH<sub>2</sub>). The synthesis method is based on the SnCl<sub>2</sub>-mediated reduction of pentaynediols prepared by early or late divergent strategies; the latter allows access to a OMe–NO<sub>2</sub> push–pull diaryl-DBA. If R<sup>1</sup> and R<sup>2</sup> are H, an over-reduced dialkynylbutatriene (DAB) with two allenyl caps was isolated instead of

# Introduction

For 15 years, the chemistry of *carbo*-mers has mainly focused on the synthesis of cyclic representatives, and more particularly of *carbo*-benzenes,<sup>[1]</sup> in order to learn and benefit from their aromatic character in the design of stable  $\pi$ -functional molecular materials.<sup>[2]</sup> Recently however, *carbo*-mers of acyclic oligomethyne chains, containing more than one dialkynylbutatriene (DAB) unit not embedded in a macroaromatic ring, were found to be more stable than anticipated, while meeting a general challenge in the chemistry of butatrienes (or [3]cumulenes).<sup>[1c]</sup> Such *carbo*-oligoacetylenes, identified generically as "1,4-PTAs", that is, 1,4-isomers of the reference polytriacetylenes (1,2-PTAs),<sup>[3]</sup> were exemplified in the perphenylated series by the DAB monomer, the di(alkynylbutatrienyl)acetylene (DaBA or DBA) dimer, and the less stable di(alkynylbutatrienylethynyl)bu-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201303169. It includes the synthesis procedures and characterization data for new compounds (including <sup>1</sup>H and <sup>13</sup>C{1H} NMR spectra and cyclic and square-wave electrochemical voltammograms), as well as a color version of Figure 7. the unsubstituted DBA. If  $R^1 = R^2 = R$ , the tetraalkynyl-DBA target was obtained, along with an over-reduced DBA product with a 12-membered 1,2-alkylidene- $1H_{2r}2H_2$ -carbo-cyclobutadiene ring. X-ray crystallography shows that all of the acyclic DBAs adopt a planar *trans-transoid-trans* configuration. The maximum UV/Vis absorption wavelength is found to vary consistently with the overall  $\pi$ -conjugation extent and, more intriguingly, with the  $\pi$ -donor character of the aryl X substituents, which varies consistently with the first (reversible) reduction potential and first (irreversible) oxidation peak, as determined by voltammetry.

tatriene (DaBEB) trimer, capped with tri(isopropyl)silyl (TIPS) stabilizing groups (Figure 1, top).<sup>[4]</sup>



Functional *carbo*-butadienes (DBAs, for dialkynyl-DiButatrienylAcetylenes)

**Figure 1.** Perphenylated *carbo*-oligoacetylenes exemplified for n = 0-3 (1,4-PTAs; E: Sii/Pr<sub>3</sub>) relative to the reference polytriacetylene (1,2-PTA) isomers (top),<sup>[3,4]</sup> and functional n = 2 derivatives exemplified for R<sup>1</sup> and R<sup>2</sup> being 4-X-C<sub>6</sub>H<sub>4</sub> (X: NH<sub>2</sub>, NMe<sub>2</sub>, indol-*N*-yl, or carbazol-*N*-yl; bottom).<sup>[5]</sup>

In the functional series, DBAs decorated with terminal *p*-aminophenyl substituents (Figure 1, bottom) were also recently described in comparison with their *carbo*-benzene counterparts.<sup>[5a]</sup> These preliminary results showed that regarding UV/Vis absorption and redox properties, the DBA (or *carbo*-butadiene) backbone is much more sensitive to substituent effects than the *p*-*carbo*-benzene core. This trend is consistent with the  $\pi$ -insulating character anticipated for an aromatic ring, with the effect being enhanced in this case by the R<sup>1</sup> $\rightarrow$ C<sub>18</sub> $\leftarrow$ R<sup>2</sup>  $\pi$ -frustration that results from the  $\pi$ -donation of the two aminophenyl R<sup>*i*</sup> substituents towards the  $\pi$ -electron-rich and soft C<sub>18</sub> *carbo*-benzene core.<sup>[5b]</sup> With consideration of the photophysical and liquid crystals properties of the parent 1,4-diaryl-substituted

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effect at the 1- and 10-positions of the expanded carbo-butadiene backbone was undertaken. The synthesis and physicochemical properties (X-ray crystal structures, electronic spectra, and voltammograms) of homoand hetero-substituted representatives bearing either donor and/or acceptor R<sup>1</sup> and R<sup>2</sup> aryl groups (Figure 1) is described hereafter. Although it gave rise unexpected  $\pi$ -conjugated to structures, substitution by nonaryl substituents (R<sup>1</sup>, R<sup>2</sup>: H,  $C \equiv C - TIPS$ ) was also achieved.



Scheme 1. The two synthetic approaches envisaged for functional carbo-butadiene targets.

### **Results and Discussion**

Two strategies were envisaged for anchoring the R<sup>1</sup> and R<sup>2</sup> substituents to the *carbo*-butadiene backbone at earlier or later stages of the synthesis from the same known triyne precursor 1.<sup>[7]</sup> The first one, inspired by the reported synthesis of the reference tetraphenylated DBA,<sup>[4]</sup> relies on the addition of disalts of 1 to selected aldehyde substrates, followed by oxidation of the resulting carbinol centers and subsequent addition of two equivalents of tri(isopropyl)silylacetylide (strategy A, Scheme 1). The alternative method is based on the intermediacy of the pentaynedione **2**, the carbonyl groups of which serve as electrophilic centers, for example, for the introduction of various 4-aminophenyl R<sup>1</sup> and R<sup>2</sup> groups (strategy B, Scheme 1).<sup>[5a]</sup> Pentaynedione **2** can be prepared in two steps from triyne **1**, so the latter is the convergence point of the two strategies (Scheme 1), with the first one (A) being more versa-

tile (for allowing the introduction of different  $R^1$  and  $R^2$  substituents) and the second one (B) diverging later (from intermediate **2**). Both strategies end up with an eliminative reduction of the ultimate pentaynediol precursors **3**.

#### Synthesis of pentaynediol DBA precursors directly from triyne 1 (strategy A)

Strategy A (Scheme 1) was first applied to the synthesis of the symmetrically substituted pentaynediols **3a-d** and to the synthesis of the unsubstituted precursor, **3e**, of pentaynedione **2**, a key intermediate of strategy B (see below). Addition of the dibromomagnesium or dilithium salt of **1** (as a mixture of two diastereoisomers) to *p*-anisaldehyde, *p*-nitrobenzaldehyde, *p*-trifluoromethylbenzaldehyde, *p*-dimethylaminobenzaldehyde, or paraformaldehyde gave the corresponding triynediols **4a**–**e** (Scheme 2). The dilithium salt of **1** was found to react selectively with all of the aldehydes except *p*-nitrobenzaldehyde, from which only undetermined polymeric products were obtained. Instead, the use of the dibromomagnesium salt of **1** allowed the bis(nitrophenyl)triynediol **4b** to be isolated in 55% yield. The double additions of **1** were found to proceed in higher yields with aldehydes than with the propargylic phenyl-ketone **5** that was previously reported to give perphenylated pentaynediol **3f** in 51% yield.<sup>[4]</sup> From stereoisomeric mixtures of triyne **1**, the triynediols **4a–e** were obtained as mixtures of diastereoisomers.

Oxidation of the secondary diols 4a-d to the corresponding diketones 6a-d was performed with MnO<sub>2</sub> in dichloromethane at room temperature. Dialdehyde 6e was reported to decompose upon purification by chromatography on silica gel,<sup>[7b]</sup> so oxidation of the primary diol 4e into pure 6e required the use



Scheme 2. Synthesis of the pentaynediols 3 a–f in three steps from triyne 1. DCM: dichloromethane; DCE: 1,2-dichloroethane; IBX: 2-iodoxybenzoic acid.



of 2-iodoxybenzoic acid in refluxing 1,2-dichloroethane.<sup>[8]</sup> Finally, addition of two equivalents of lithium tri(isopropyl)silylacetylide to diketones 6a-c and dialdehyde 6e afforded the corresponding pentaynediols 3ac and 3e in 57-90% yield. In contrast, by using a similar procedure with dimethylaminophenylketone 6d, pentaynediol 3d could be neither isolated nor observed (Scheme 2). The electrophilicity of the carbonyl functionalities of **6d** is dramatically reduced by phenylogous  $\pi$ -donation from the dimethylamino substituents,<sup>[5a]</sup> so the synthesis of 3d was addressed through the alternative strategy B (Scheme 1; see below).

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Scheme 3. Synthesis of the dissymmetrically substituted pentaynediol 3 g.

Strategy A was also applied to the preparation of the dissymmetrically substituted pentaynediol **3g**, the anticipated precursor of a push-pull *carbo*-butadiene bearing a  $\pi$ -donating anisyl group and a  $\pi$ -accepting nitrophenyl group (Scheme 3). Therefore, the anisyl group was first anchored by addition of the monolithium salt of **1** to *p*-anisaldehyde, to give the intermediate monoalcohol **7** in 65% yield. The nitrophenyl group was then introduced by addition of the dilithium salt of **7** to *p*nitrobenzaldehyde, with the resulting triynediol **4g** being isolated in 75% yield. The last two steps in the synthesis of pentaynediol **3g** were based on the same procedures as those used for the preparation of the homosubstituted counterparts

**3 a–c** and **3 e** (Scheme 2 and Scheme 3): oxidation of the secondary carbinol centers of **4 g** with  $MnO_2$  in 75% yield, followed by double addition of lithium tri(isopropyl)silylacetylide to the resulting diketone **6 g** to give **3 g** in 93% yield.

#### Synthesis of pentaynediol DBA precursors via pentaynedione 2 (strategy B)

Pentaynedione **2**, the key intermediate of strategy B (Scheme 1), can be quantitatively prepared by  $MnO_2$ -mediated oxidation of pentaynediol **3**e, itself obtained in three steps from triyne **1** (Scheme 2 and Scheme 4).<sup>[5a]</sup> Double additions of organolithium or -magnesium reactants to **2** were exemplified with *p*-aminophenyl nucleophiles in a complete study that has been detailed elsewhere and will not be discussed herein.<sup>[5a]</sup> In summary, however, whereas 1-(4-lithiophenyl)-1*H*-indole and 9-(4-lithiophenyl)-9*H*carbazole afforded the corresponding pentaynediols in 85 and 82% yields after isolation, respectively (Scheme 4, left),<sup>[5b]</sup> the reaction of **2** with 4-R<sub>2</sub>N-phenylmetals (R: Me, SiMe<sub>3</sub>) did not allow the isolation of the pentaynediol products in a pure state. Nevertheless, by using the Grignard reactants of the *p*bromoaminophenyl derivatives, the method allowed the formation and partial characterization of the silica-gel-sensitive di(aminophenyl)pentaynediol derivatives **3d** (R: Me; not detected with strategy A: see Scheme 2) and **3h** (R: SiMe<sub>3</sub> or H).



Scheme 4. Preparation of the pentaynedione intermediate 2 for the late-divergent strategy B (Scheme 1), and reactions of 2 with C-nucleophiles.<sup>[5a]</sup>



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These compounds could, however, be used in the crude state for the reduction step to the di(aminophenyl)-*carbo*-butadiene targets **8d** and **8h** (see below).<sup>[5a]</sup>

The strategy was also used to anchor non-aryl substituents on the DBA backbone by addition of lithium tri(isopropyl)silylacetylide to pentaynedione **2**. Heptaynediol **3** i, with four tri(isopropyl)silylethynyl arms, was thus isolated in 80% yield (Scheme 4, right).

# Preparation of *carbo*-butadienes by eliminative reduction of pentaynediols

Reduction of the pentaynediols to the *carbo*-butadiene targets was performed with the classical acidic reductive system, SnCl<sub>2</sub>/HCl (Scheme 5). As previously reported, the crude diols



Scheme 5. Preparation of functional *carbo*-butadienes by  $SnCl_2$ -mediated reduction of pentaynediol precursors. For 8d and 8h, see ref. [5a]; for 8f, see ref. [4].

**3 d** and **3 h**<sup>[5a]</sup> and the tetraphenyl reference **3 f**<sup>[4]</sup> were converted into the DBAs **8 d**, **8 h**, and **8 f** in 29, 53, and 95% yield, respectively. Likewise, after optimization of the procedure, similar treatment of the pentaynediols **3a–c** and **3g** led to the *carbo*-butadienes **8a–c** and **8g** as the main products of the crude reaction mixtures, according to <sup>1</sup>H NMR spectroscopic analyses. The quite low isolated yields for **8b**, **8d**, and **8g** (approximately ( $25 \pm 5$ )%) are due to the poor solubility of the compounds, which makes them intractable by chromatography only and thus requires recrystallizations of the most pure fractions. The reductions were performed in dichloromethane, except for the preparation of the bis(*N*,*N*-dimethylaminophenyl)-*carbo*-butadiene **8d**, the formation of which required the use of diethyl ether as the solvent.<sup>[5a]</sup>

All of the 1,10-diarylated *carbo*-butadienes were obtained as mixtures of *cis–cis, cis–trans*, and *trans–trans* isomers, as evidenced for **8b** by three deshielded <sup>1</sup>H NMR doublet signals of the *meta* protons of the 4-nitrophenyl substituents (in a 20:23:57 ratio going upfield: see Figure 2). It can be assumed that the most intense doublet corresponds to the less strained *trans–trans* isomer of **8b**.



**Figure 2.** <sup>1</sup>H NMR spectroscopic evidence of the three isomers, in a 20:23:57 integrated ratio, of the *carbo*-butadiene **8b** based on the deshielded *meta* protons (H3) of the 4-nitrophenyl substituents (CDCl<sub>3</sub>, 400 MHz).

From solutions in suitable solvents, the seven *carbo*-butadienes **8a–d** and **8f–h** gave monocrystals suitable for X-ray diffraction analysis (Figure 3). All of them crystallized in the all-



**Figure 3.** Molecular views of the all-*trans* isomers of **8a–d**, **8 f**, **8 f**–**8 h** in the crystal state (for clarity, the H atoms are omitted). All of the molecules appear centrosymmetric (even **8 g** because of a NO<sub>2</sub>/OMe disorder, which is artificially lifted here), and the 16 successive atoms of the common dialkynyl-DBA chain are numbered as Si1–C1–C2–C3–C4–C5–C6–C7–C7A... and the symmetric CiA ( $6 \ge i \ge 1$ ) and Si1A (Table 1). For **8 d** and **8 h**, see ref. [5a]; for **8 f**, see ref. [4].

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trans (that is, trans-transoid-trans) configuration, in a consistent manner with the proposed interpretation of the major signals in the <sup>1</sup>H NMR spectrum of **8b** (Figure 2). Similar values were obtained for the bond lengths and bond angles of the common DBA backbone (Table 1). All of the molecules were found to be centrosymmetric, or quasi-centrosymmetric for **8g** bearing the different but similar OMe and NO<sub>2</sub> substituents, which exchange in a crystallographic disorder.

Table 1. Selected crystallographic data for the carbo-butadienes 8a-d, 8 f-i, and 10. <sup>[a]</sup>									
	8 a	8 b	8 c	8 d	8 h	8 f	8 g	8i	10
space group	P1	P1	P1	P1	PĪ	ΡĪ	P1	P1	C2/c
R [%]	5.49	4.99	7.04	4.48	4.76	5.57	5.93	4.22	9.02
Bond lengths	[A]	1 0 2 7	1 0 2 0	1 0 2 0	1 0 2 7	1 0 4 0	1 0 2 2	1 0 4 2	1 0 2 0
	1.833	1.837	1.829	1.829	1.837	1.840	1.833	1.842	1.830
CI-C2	1.208	1.207	1.209	1.203	1.207	1.207	1.208	1.201	1.204
C2-C3	1.433	1.435	1.433	1.433	1.430	1.432	1.430	1.426	1.421
C3–C4	1.358	1.351	1.352	1.354	1.358	1.351	1.359	1.352	1.351
C4–C5	1.232	1.237	1.242	1.230	1.235	1.237	1.233	1.234	1.245
C5–C6	1.359	1.356	1.361	1.357	1.358	1.354	1.358	1.356	1.372
C6–C7	1.412	1.413	1.418	1.413	1.414	1.418	1.410	1.418	1.421
C7–C7A	1.209	1.201	1.204	1.206	1.210	1.203	1.207	1.200	1.139
Si1A–C9	-	-	-	-	-	-	-	1.846	1.899
C8–C9	-	-	-	-	-	-	-	1.205	1.288
C8–C3	-	-	-	-	-	-	-	1.429	1.501
C8–C8A	-	-	-	-	-	-	-	-	1.540
Bonds angles	[°]								
C2–C3–C4	117.4	117.2	117.4	116.1	117.0	116.7	117.6	121.2	123.8
C5–C6–C7	117.8	119.6	117.5	116.9	117.7	117.9	118.2	117.5	112.2
C4–C3–C8	-	-	-	-	-	-	-	122.0	116.8
C6–C7–C7A	-	-	-	-	-	-	-	-	162.6
C4–C5–C6	-	-	-	-	-	-	-	-	169.6
C3–C4–C5	-	-	-	-	-	-	-	-	168.9
[a] Bond lengths [Å] and bond angles [°] measured (within estimated standard deviation errors) with Mercury 3.1.1 as the graphic interface. Mo- lecular views and numbering of the pseudo-centrosymmetic DBA back- bone are shown in Figure 3 and Figure 5. For <b>8d</b> and <b>8h</b> , see ref. [5a]; for <b>8f</b> , see ref. [4]; and for crystallographic parameters of the other com- pounds see Table 3.									

When applied to the bis-secondary pentaynediol **3e**, the reduction procedure did not afford the unsubstituted *carbo*-butadiene target **8e** ( $R^1 = R^2$ : H). Instead, the 1,4-di(allenylethy-nyl)butatriene **9** was isolated in 42% yield (Scheme 6). The unprecedented structure of **9** extends the possible caps of DABs from trialkylsilyl, aryl, alkenyl, and butatrienyl caps (the latter in



Scheme 6. Synthesis of the diallenyl-capped DAB 9.

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*carbo*-benzene Kékulé forms) to allenyl caps<sup>[9]</sup> and resembles the core structure of the recently reported dialkynyl-*carbo*-hexatriene.<sup>[4]</sup> In spite of poor stability, even at low temperature, which thus prevented selective crystallization for X-ray diffraction analysis, the diallene **9** could be unambigously identified by MS, NMR spectroscopy, and UV/Vis spectroscopy (Figure 4 and Figure 7). In particular, the characteristic NMR signals of the allenyl caps are the <sup>1</sup>H resonances between  $\delta$ =5.36 and 5.47 ppm for the four sp<sup>2</sup>-CH units (Figure 4) and a <sup>13</sup>C resonance at  $\delta$ =216 ppm for the central sp-C atom.



Figure 4. <sup>1</sup>H NMR spectrum of the diallenyl-capped DAB 9 (CDCl<sub>3</sub>, 400 MHz).

With the view of preparing the 1,10-tetraalkynyl-DBA 8i, pentaynediol 3i was subjected to treatment with SnCl<sub>2</sub>/HCl (Scheme 7). However, as described above for 3e, this acidic reductive system was found to be impracticable because substrate 3i also bears non-aryl external substituents (unlike 3a-d and 3 f-h). Standard conditions, which consisted of the addition of SnCl<sub>2</sub> and ethereal HCl to a solution of **3i** in dichloromethane at -78°C, followed by a slow warming up of the reaction mixture (in a cold bath) before quenching with aqueous NaOH, produced only undetermined polymeric materials. Target 8i could, however, be obtained by using a modified procedure involving a fast warming up of the reaction mixture and careful "visual monitoring": when aqueous NaOH was added at the dark-red stage (approximately 12 min after addition of HCl and stirring at room temperature), two main spots were observed on TLC plates, and the corresponding products could be separated by chromatography on silica gel. The less polar red fraction afforded the target acyclic tetraalkynyl-carbobutadiene 8i in 15% yield. The more polar orange fraction turned out to be the over-reduced cyclic DBA 10, which was isolated in 16% yield. This strained structure was assigned on the basis of MS and NMR spectroscopy and was confirmed by X-ray crystallography (Figure 5; see below). However, the reaction selectivity and yields for products 8i and 10 proved to be highly sensitive to the exact conditions used. If the guenching





**Scheme 7.** Reactivity of the heptaynediol **3 i** with the SnCl<sub>2</sub>/HCl reducing system (top), and formal relationship of **10** with the antiaromatic (unknown) *carbo*-cyclobutadiene derivative (bottom).<sup>[10]</sup>





**Figure 5.**  $C_2$ -symmetric molecular diagrams of DBAs **8i** and **10** in the crystal state (for clarity, the H atoms are omitted). The 16 atoms of the dialkynyl-DBA chains are numbered as Si1–C1–C2–C3–C4–C5–C6–C7–C7A... and the symmetric CiA ( $6 \ge i \ge 1$ ) and Si1A (Table 1).

was performed at an earlier stage (after a reaction time shorter than 10 min), 8i was obtained in only 8% yield, in a mixture



with 50% unreacted diol **3i**. If the reaction was prolonged over more than 15 min, a considerable amount of polymeric material was produced. These observations suggest that the cyclic DBA **10** arises from a subsequent reductive cyclization of the primary product **8i** and tends to release its strain by polymerization under the acidic conditions required for the reduction process.

The structures of **8i** and **10** were confirmed by X-ray crystallography (Figure 5, Table 1, and Table 3 in the Experimental Section), but whereas the data for **8i** resemble those of the homologous diarylated DBAs **8a– d** and **8f–h** those for **10**, although less accurate (R=9%), reveal unique features. The 12-

 $π_z$  electron macrocycle of **10** can indeed be regarded as a dicarbene-stabilized form of the *carbo*-cyclobutadiene ring, which is predicted to be strongly antiaromatic by the Hückel rules and by various energetic or magnetic indices calculated from the DFT-calculated structure of the parent unsubstituted *carbo*-cyclobutadiene (see explanative illustration at the bottom of Scheme 7).<sup>[10]</sup> It is noteworthy that the two C=CHTIPS bonds of the 1,2-alkylidene-1*H*<sub>2</sub>,2*H*<sub>2</sub>-*carbo*-cyclobutadiene **10** are coplanar and almost perpendicular to the endocyclic butatriene units of the C12 macrocycle (dihedral angle ≈ 99°), which makes the latter just nonaromatic by cutting the cyclic  $π_z$  conjugation.

#### Absorption spectroscopy of functional carbo-butadienes

The UV/Vis absorption spectra of the functional DBAs 8a-d and 8 f-i were recorded in chloroform solution at room temperature (Figure 6). All of the chromophores display similar spectral profiles, with an intense absorption band at high wavelengths (with molar absorption coefficients ( $\varepsilon$ ) in the range 40000–110000 Lmol<sup>-1</sup> cm<sup>-1</sup>) and several secondary bands at lower wavelengths. The range of variation of the  $\lambda_{max}$ values is 117 nm, with two extreme values for the bis-(tri(isopropyl)silylethynyl) derivative **8i** ( $\lambda_{max}$  = 552 nm) and the bis(dimethylaminophenyl) derivative **8d** ( $\lambda_{max} = 669$  nm). The maximum absorption wavelength is thus observed for the compound with the most  $\pi$ -donating R<sup>1</sup> and R<sup>2</sup> substituents on the DBA backbone, that is the N,N-dimethylaminophen-4-yl groups of 8d.<sup>[5a]</sup> A bathochromic shift of 102 nm is induced by substitution of the p-CH positions of the diphenyl DBA reference **8 f** ( $\lambda_{max}$  = 567 nm) with NMe<sub>2</sub> groups in **8 d**. In a related monobutatrienic DAB series,<sup>[9]</sup> a similar bathochromic shift of 104 nm was reported by Diederich and co-workers upon replacement of the phenyl groups by dimethylaminophenyl





Figure 6. UV/Vis absorption spectra of DBAs 8a-d and 8f-i (in CHCl<sub>3</sub>). For 8d and 8h, see ref. [5a]; for 8f, see ref. [4].

groups.<sup>[9a]</sup> Apart from the dimethylaminophenyl derivative **8d** ( $\lambda_{max} = 669 \text{ nm}$ ) and the non-methylated diaminophenyl derivative **8h** ( $\lambda_{max} = 622 \text{ nm}$ ),<sup>[5a]</sup> two families of DBAs with similar  $\lambda_{max}$  values can be distinguished: the **8a,b,g** family with  $\lambda_{max} = (600 \pm 9) \text{ nm}$  and the **8c,f,i** family with  $\lambda_{max} = (559.5 \pm 7.5) \text{ nm}$ . Just like **8d** and **8h**, the first family is constituted by aryl-substituted DBAs in which the 4-X-C<sub>6</sub>H<sub>4</sub> aryl conjugation extends beyond the C<sub>6</sub>H<sub>4</sub> core to a  $\pi$ -conjugating X substituent, either  $\pi$  donating (OMe) or  $\pi$  accepting (NO<sub>2</sub>). Shrinking of the  $\pi$ -conjugation extent to the C<sub>6</sub>H<sub>4</sub> core only in **8f** (X: H) and **8c** (X: CF<sub>3</sub>) results in a 25 nm hypsochromic shift down to  $\lambda_{max} = (566.5 \pm 0.5) \text{ nm}$ . This second family is completed and bounded by the alkynyl-substituted DBA **8i**, which exhibits the shortest conjugation extent and, thus, the lowest maximum absorption wavelength at  $\lambda_{max} = 552 \text{ nm}$ .

Relative to those of the above isostructural DBAs (Figure 6), the peculiar products **9** and **10** display quite different UV/Vis



**Figure 7.** UV/Vis spectra of the diallenyl-capped DAB **9** and the cyclic DBA **10** (in CHCl<sub>3</sub>). For a color version, see the Supporting Information.

absorption profiles (Figure 7). The diallenyl-capped DAB 9 appears as a strongly absorbing dye in the range 250-500 nm, probably because of a broad spectral superimposition of the conjugated allene and butatriene chromophoric units in the various stereoisomers or conformers. The cyclic DBA 10 exhibits a maximum absorption wavelength at  $\lambda_{max} = 402 \text{ nm}$ , a much smaller value than the 552 nm lower boundary attained for 8i in the acyclic DBA series. This hypsochromic shift for 10 is actually consistent with a further cut of the conjugation extent with respect to the acyclic dehydro precursor 8i: the C=CH-TIPS bonds, which corre-

spond to two of the four C  $\equiv$  C–TIPS bonds in **8***i*, are indeed no longer  $\pi$ -conjugated with the butatriene units of the original DBA in the constrained C12 macrocycle of **10** (with a dihedral angle of 99°; Figure 5). The  $\lambda_{max}$  value of **10** actually lies in the range of  $\lambda_{max}$  values of isolated DABs ( $\lambda_{max} = (400 \pm$ 25) nm).<sup>[4,9c]</sup> Nevertheless, the UV/Vis spectrum of **10** also exhibits a weak band at 514 nm (Figure 7), which is reminiscent of those bands observed in other macrocyclic  $\pi$ -conjugated oligoacetylenics like *carbo*-benzenes and tentatively attibuted to vibronic coupling.<sup>[2d,5b]</sup>

#### Electrochemistry of functional carbo-butadienes

The electrochemical properties of the DBAs 8a-d and 8fi and the derivatives 9 and 10 were investigated by squarewave (SWV) and cyclic (CV) voltammetry (Table 2). The DBAs 8a-d and 8f-i exhibit similar reduction behaviors, with three reduction waves for most of them, except for 8c, which undergoes six reductions steps, and 81, which undergoes only two. A single reduction was found to be reversible for 8a and 8f, whereas two reversible reductions were observed for all of the other DBAs. In the case of the push-pull DBA 8g, the two first processes became reversible only at high scan rates (5  $V s^{-1}$ ). As compared to related monobutatrienic DAB homologues,<sup>[9c]</sup> the increase of the  $\pi$ -conjugation extent in the dibutatrienic DBAs induces a greater ease of reduction: this is illustrated qualitatively by the appearance of a second reversible reduction wave in the DBA series and quantitatively by the relative reduction potentials of the diphenylated DBA 8f ( $E_{1/2}$ = -0.80 V) relative to those of the corresponding diphenylated DAB ( $E_{1/2} = -1.57$  V). In the diaryl-DBA series, the first reduction potential varies from -0.95 V (8d) to -0.52 V (8b), in a manner consistent with the acceptor character of the 4-X- $C_6H_4$  aryl substituent: **8d** (X: NMe<sub>2</sub>) < **8h** (X: NH<sub>2</sub>) < **8a** (X: OMe) < 8f (X: H) < 8c (X: CF<sub>3</sub>)  $\approx 8g$  (X: NO<sub>2</sub>, OMe) < 8b (X: NO<sub>2</sub>). It is noteworthy that the first reduction potential of the

Table 2. CV and SWV data for DBAs 8a-d, 8f-i, and 10 and DAB 9. <sup>[a]</sup>							
	Reduction			Oxidation			
	$E_{1/2} [V]/\Delta E_{p}$ [mV] <sup>[b]</sup>	I <sub>pox</sub> / I <sub>pred</sub> <sup>[c]</sup>	E <sub>p</sub> [V] <sup>[d]</sup>	$E_{1/2} [V]/\Delta E_{p}$ [mV] <sup>[b]</sup>	$I_{\rm pred}/I_{\rm pox}$	E <sub>p</sub> [V] <sup>[d]</sup>	
8a	-0.88/99	1.03	-1.22	-	_	0.95	
			-1.45			1.03	
8b	-0.52/96	0.99	-1.71	-	-	1.39	
	-1.24/114	1.01					
8c	-0.65/93	1.01	-1.15	-	-	1.31	
	-0.87/92	1.02	-1.59			1.59	
			-1.71				
			-1.83				
8d	-0.95/73	1.06	-1.55	0.43/63	0.99	1.65	
	-1.25/64	0.78					
8h	-0.92/73	1.12	-1.53	0.51/63	0.87	1.70	
	-1.26/64	0.96					
8 f	-0.80/106	1.20	-1.12	-	-	0.95	
			-1.37			1.15 <sup>(a)</sup>	
8g	-0.62/91 <sup>[e]</sup>	1.32	-1.66	1.06/93 <sup>[e]</sup>	1.10	1.34	
	-0.78/88 <sup>[e]</sup>	0.66					
8i	-0.65/94	0.97	-	1.29/95	0.97	-	
	-0.94/115	0.98					
9	$-1.16/100^{[f]}$	1.28	-1.42	-	-	1.03	
			-1.55				
10	-1.15/108	0.87	-1.48	1.21/103 <sup>[g]</sup>	1.00	-	
			-1.66				

[a] Data for **8d** and **8h** in ref. [5a]; data for **8f** in ref. [4]. Measurements were performed at room temperature in dichloromethane; supporting electrolyte:  $[n-Bu_4N][PF_6]$  (0.1 m); working electrode: Pt; reference electrode: saturated calomel electrode (SCE; 0.242 V versus the hydrogen electrode); scan rate:  $0.2 V s^{-1}$  unless otherwise noted. [b]  $E_{I_6} = [E_{pc} + E_{pa}]/2$ , the arithmetic mean of anodic and cathodic peak potentials;  $\Delta E_p$ : CV peak-to-peak separation for reversible processes. [c]  $I_{pox}/I_{pred}$ : absolute current ratio for reversible processes measured by CV. [d]  $E_p$ : half-wave potential determined by SWV for irreversible processes. [e] Becomes reversible at a scan rate of  $5 V s^{-1}$ . [f] Becomes reversible at a scan rate of  $1 V s^{-1}$ . [g] The formation of radicals is observed at high scan rates, but the reversibility of the first oxidation remains unchanged.

dialkynyl-DBA **8i** (-0.65 V) is close to those of the acceptorsubstituted diaryl-DBAs **8c** and **8g**, probably because of the  $\alpha$  effect of the silicon atoms, which is supposed to stabilize the reducing electron at the terminal C atoms of the four triple bonds of **8i**.

In the oxidation regime, the *carbo*-butadienes **8a–d** and **8f-i** undergo one or two oxidation steps, most of them being irreversible. Nevertheless, by symmetry with respect to the reversible half-wave potentials recorded in the reduction regime (groups that stabilize cations generally destabilize anions, and conversely), the first oxidation peak potential varies from + 0.43 V (**8d**) to + 1.39 V (**8b**), in a manner consistent with the donor characteristics of the 4-X-C<sub>6</sub>H<sub>4</sub> aryl substituent: **8d** (X: NMe<sub>2</sub>, rev.) < **8h** (X: NH<sub>2</sub>, rev.) < **8a** (X: OMe)  $\approx$  **8f** (X: H) < **8g** (X: NO<sub>2</sub>, OMe, rev.) < **8f** (X: H, rev.) < **8c** (X: CF<sub>3</sub>) < **8b** (X: NO<sub>2</sub>). Rankings are for irreversible waves, unless otherwise noted as "rev.").

In spite of a moderate stability, the diallenyl-DAB **9** and cyclic-DBA **10** could also be studied by CV and SWV. In the reduction regime, both of them exhibit the same behavior, with one reversible reduction at almost identical potentials (approximately -1.15 V) and two irreversible counterparts. In the oxi-

dation regime, a single wave was recorded for both **9** and **10** (Table 2). The reversibility of the reduction of **10** might be correlated with the non(anti)aromatic character of a  $13-\pi_z$ -electron *carbo*-cyclobutadienide ring,<sup>[11]</sup> which exhibits an extended conjugation (relative to the neutral substrate) after possible planarization of the macrocyclic radical anion. The formation of the latter would indeed be consistent with the voltammetric observations at high scan rates (Table 2).

## Conclusion

The disclosed results establish the structural variability of stable dibutatrienic species outside a macroaromatic environment, like the Kékulé-resonant *carbo*-benzene ring.<sup>[1c]</sup> They provide an experimental basis for the design of a well-defined class of  $\pi$ -extended organic molecules with promising optical or (opto)electronic properties. Following the carbo-mer principle,<sup>[1]</sup> further targets are indeed naturally suggested by the recognized properties of parent butadiene derivatives. For example, the  $E, E \rightarrow Z, Z$  photoisomerization ability of 1,4-diphenylbutadiene<sup>[12]</sup> would deserve comparison with that of the corresponding carbo-butadiene, the individual 1,4-disubstituted butatriene units of which are supposed to exhibit a much lower cis-trans isomerization barrier.<sup>[9b,c]</sup> Other natural carbo-merization candidates (that is, molecules with specific properties that might be refined further in the carbo-meric version and therefore justify synthesis efforts toward the latter) are 1,1,4,4-tetraphenylbutadiene (TPB), an electroluminescent dye commonly used as a blue-emitting wavelength shifter from the UV/Vis spectral region (Scheme 8),<sup>[13]</sup> and, in the functional series, the 1,4-di(p-aminophenyl)butadiene (DAPB) chromophores.<sup>[5a, 14]</sup> In the proposed *carbo*-meric targets, the external  $C \equiv C-TIPS$ arms of 8a-g and 8i would no longer be essential, and auxiliary substitution of the internal, but distant, Csp<sup>2</sup> centers, a stabilizing factor for the butatriene units,<sup>[1c]</sup> would not induce torsion of the DBA motif: these targets could thus achieve optimal  $n \pi$ -conjugation over ten carbon atoms in still allowed quasiplanar conformations (Scheme 8, Figure 3).



**Scheme 8.** Simple DBA target suggested by the *carbo*-mer principle and the known electro-optical properties of the parent molecule (1,1,4,4-tetraphenyl-1,3-butadiene in this case).<sup>[13]</sup>

# **Experimental Section**

#### General

THF and diethyl ether were dried and distilled over sodium/benzophenone; pentane and dichloromethane were dried and distilled over  $P_2O_5$ . All other reagents were used as commercially available. In particular, commercial solutions of *n*BuLi were 2.5 m in hexane,





solutions of ethylmagnesium bromide were 3 m in THF, and solutions of HCl were 2 m in diethyl ether. Previously described procedures were used for the preparation of  $1^{[7]}_{,} 2^{[5]}_{,} 3e^{[5]}_{,} 3f^{[4]}_{,} 4e^{[7]}_{,}$  ${\bf 5},^{\rm [9c]}\,{\bf 6}\,{\bf e},^{\rm [7]}\,{\bf 8}\,{\bf d},^{\rm [5]}\,{\bf 8}\,{\bf h},^{\rm [5]}$  and  ${\bf 8}\,{\bf f}.^{\rm [4]}$  All of the reactions were carried out under a nitrogen or argon atmosphere by using Schlenk and vacuum-line techniques. Column chromatography was carried out on silica gel (60 P, 70-200 mm). Silica gel thin-layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following routine analytical instruments were used: mass spectrometry: Quadrupolar Nermag R10–10H spectrometer; UV/Vis spectroscopy: Perkin-Elmer UV/Vis Win-Lab Lambda 35 spectrometer; <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy: Bruker DPX 300, Avance 300, Avance 400, Avance 400WB, or Avance 500 spectrometers. Most of the NMR spectra were recorded in CDCl $_3$  solutions. NMR chemical shifts  $\delta$ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz. <sup>13</sup>C{<sup>1</sup>H} chemical shifts refer to <sup>13</sup>C NMR spectra recorded under broad band decoupling of the <sup>1</sup>H nuclei. The synthesis procedures and characterization data for new compounds can be found in the Supporting Information.

#### Voltammetry

Voltammetric measurements were carried out with an Autolab PGSTAT100 potentiostat controlled by GPES 4.09 software. Experi-

ments were performed at room temperature in a home-made airtight three-electrode cell connected to a vacuum/argon 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 approximately 1 cm<sup>2</sup> apparent surface area. The working electrode was a Pt microdisk (0.5 mm diameter) or a glassy carbon microdisk (1 mm diameter). The supporting electrolyte [nBu<sub>4</sub>N][PF<sub>6</sub>] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled prior to use. The solution concentrations were typically 10<sup>-3</sup> M for the studied molecule and 0.1 M for the supporting electrolyte. Before each measurement, the solutions were degassed by bubbling argon, and the working electrode was polished with a polishing machine (Presi P230). Typical instrument parameters for square-wave voltammograms were: SW frequency, f = 20 Hz; SW amplitude, Esw = 20 mV; scan increment,  $\delta F = 0.5 \text{ mV}.$ 

#### Crystallography

X-ray intensity data of crystals of **8a–c**, **8g**, **8i**, and **10** were collected at 193(2) K on a Bruker-AXS APEX II diffractometer by using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics and graphite-monochromated Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å) by using  $\Phi$  and  $\Omega$  scans. The data were integrated with SAINT software, and an empirical absorption correction was applied with the

Table 3. Crystallographic data and structural refinement parameters for 8a-c, 8g, 8i and 10.								
	8a	8 b	8 c	8 g	8i	10		
initial code	ar216m		ar454m		ar334bism	ar328m		
formula	C <sub>58</sub> H <sub>66</sub> O <sub>2</sub> Si <sub>2</sub>	$C_{56}H_{60}N_2O_4Si_2$	$C_{58}H_{60}F_6Si_2$	$C_{57}H_{63}NO_3Si_2$	C <sub>66</sub> H <sub>94</sub> Si <sub>4</sub>	C <sub>66</sub> H <sub>97</sub> O <sub>0.5</sub> Si <sub>4</sub>		
M <sub>r</sub>	851.29	881.24	927.24	866.26	999.77	1010.80		
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic		
space group	PĪ	РĪ	ΡĪ	РĪ	РĪ	C2/c		
a [Å]	7.7665(6)	7.5677(5)	7.6358(10)	a7.6332(8)	11.1387(9)	14.5221(14)		
<i>b</i> [Å]	7.8099(5)	7.8409(5)	18.453(2)	7.7812(9)	12.1237(10)	19.685(2)		
c [Å]	21.4670(16)	21.2471(14)	19.817(2)	21.635(2)	14.3424(11)	c23.699(2)		
α [°]	95.546(2)	96.902(3)	103.407(7)	97.045(5)	70.552(3)	90		
β [°]	96.993(3)	93.895(3)	99.615(6)	95.339(5)	72.040(3)	102.284(3)		
γ [°]	94.385(3)	94.542(3)	97.888(6)	94.087(5)	64.835(3)	90		
V [ų]	1281.22(16)	1243.86(14)	2632.6(6)	1265.4(2)	1621.1(2)	6619.6(11)		
Ζ	1	1	2	1	1	4		
$d_{\text{calcd}} [\text{g cm}^{-1}]$	1.103	1.176	1.170	1.137	1.024	1.014		
$\mu$ [mm <sup>-1</sup> ]	0.109	0.118	0.124	0.113	0.127	0.125		
F(000)	458	470	980	464	546	2212		
crystal size [mm <sup>3</sup> ]	$0.50 \times 0.20 \times 0.02$	0.26×0.10×0.02	0.26×0.04×0.01	$0.70 \times 0.30 \times 0.02$	$0.32 \times 0.20 \times 0.04$	0.34×0.20×0.02		
heta range [°]	2.70-26.40	5.21-25.68	5.12-27.10	5.15-25.35	5.13-27.10	5.10-24.71		
index ranges	$-9 \leq h \leq 9$	$-9 \leq h \leq 8$	$-9 \leq h \leq 9$	$-9 \leq h \leq 7$	$-14 \le h \le 14$	$-17 \le h \le 17$		
	$-9 \leq k \leq 9$	$-9 \leq k \leq 9$	$-23 \le k \le 23$	$-9 \leq k \leq 8$	$-15 \le k \le 15$	$-23 \le k \le 23$		
	$-26 \le l \le 26$	$-25 \le l \le 25$	$-25 \le l \le 25$	$-26 \le l \le 26$	−17 <i>≤l≤</i> 18	$-27 \le l \le 27$		
refins collected	18998	22870	66461	16685	38 261	58357		
independent reflns	5225	4687	11 5 2 1	4577	7095	5599		
	[R(int) = 0.0478]	[ <i>R</i> (int) = 0.0665]	[R(int)=0.1613]	[R(int) = 0.0495]	[ <i>R</i> (int) = 0.0325]	[ <i>R</i> (int) = 0.0782]		
$\theta_{\max}$ [%]	99.2	98.9	99.1	98.5	99.1	98.9		
max-min transmission	0.9978-0.9476	0.9976-0.9699	0.9988-0.9685	0.9977-0.9250	0.9949–0.9605	0.9975–0.9586		
data/restraints/	5225/35/304	4687/0/295	11 521/334/738	4577/117/324	7095/78/354	5599/913/648		
parameters								
GOF on F <sup>2</sup>	1.020	1.016	0.978	1.036	1.026	1.024		
final R indices $[I > 2\sigma(I)]$	R1 = 0.0549,	R1 = 0.0499,	R1 = 0.0704,	R1 = 0.0593,	R1=0.0422,	R1 = 0.0902,		
	wR2=0.1223	wR2 = 0.0960	wR2=0.1325	wR2=0.1365	wR2=0.1084	wR2=0.2386		
R indices	R1 = 0.0937,	R1=0.1017,	R1=0.2371,	R1 = 0.0998,	R1=0.547,	R1 = 0.1592,		
(all data)	wR2=0.1403	wR2=0.1134	wR2=0.1816	wR2=0.1559	wR2=0.1167	wR2=0.2902		
largest diff. peak/hole [e Å <sup>-3</sup> ]	0.205/-0.229	0.246/-0.208	0.260/-0.202	0.459/-0.314	0.348/-0.296	0.257/—0.206		

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SADABS program.<sup>[15]</sup> The structures were solved by direct methods, with SHELXS-97 software, and refined by using the full-matrix least-squares method on  $F^{2,[16]}$  All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. Crystallographic data and structural refinement parameters are listed in Table 3, and molecular views are shown in Figures 3 and 5. CCDC 951898 (**8a**), 951902 (**8b**), 951901 (**8c**), 951903 (**8g**), 951900 (**8i**) and 951899 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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