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En route to a dianilinyl-substituted *carbo*-cyclohexadiene with promising electrical properties

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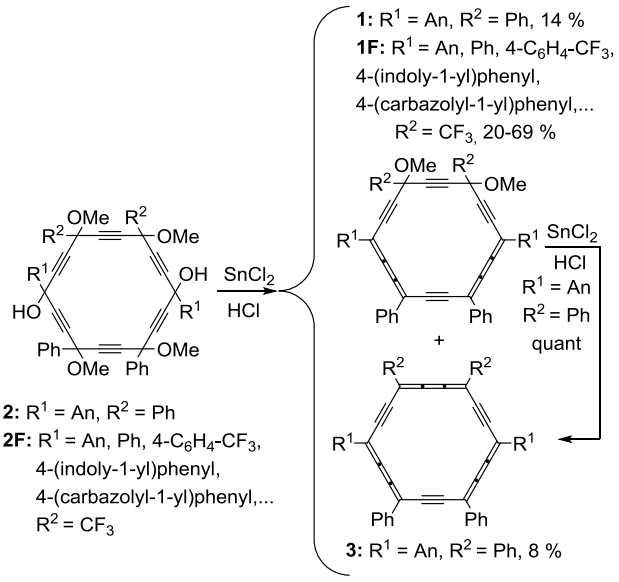
The macro-aromatic *carbo*-benzene core *para*-disubstituted by 4-anilinyl groups is known to be an efficient single-molecule conductor, exhibiting a conductance of 106 nS measured by the scanning tunneling microscopy-break junction technique. The linear *carbo*-butadiene analogue bearing the same anilinyl substituents was found to be less efficient, with a conductance of 2.7 nS. The reason of this difference could be elucidated through the study of the charge transport properties of a cyclically locked *carbo*-butadiene core in a *carbo*-cyclohexadiene derivative. In this paper, advances in the synthesis of this challenging dianilinyl-substituted *carbo*-cyclohexadiene are presented.

Introduction

After the first example of *carbo*-cyclohexadiene **1** [1,2], a substituted 1,3-cyclohexadiene isolated as a side product of the incomplete reductive aromatization of the hexaoxy[6]pericyclyne **2** [3] to the *para*-dianisyl-*carbo*-benzene **3** [1,4], a series of 1,10-diversely substituted *carbo*-cyclohexadienes **1F** was very recently accessed through a specific design [5]. This strategy is based on the introduction of trifluoromethyl substituents at two adjacent vertices of [6]pericyclynic precursors **2F**, thus preventing the formation of one of the three butatriene moieties in the corresponding *carbo*-benzenes during reductive treatment with $SnCl_2$/HCl (**Scheme 1**).

Recent studies by the scanning tunneling microscopy-break junction (STM-BJ) technique [6] evidenced the remarkable single-molecule conductance (SMC) of anilinyl-substituted *carbo*-mers and in particular of *carbo*-benzene **4** exhibiting a SMC value of 106 nS over 2 nm

[7]. For comparison, this value is *ca* ten times the conductance of a shorter hexabenzocoronene analogue [8], and *ca* 40 times that of the acyclic dianilinyl-*carbo*-butadiene analogue **5** of similar length (≈ 1.9 nm) [4g, 9] (**Figure 1**). This large difference in conductance between **4** and **5** can be proposed to be due to topological and/or geometrical features, *ie* to the participation of a single conduction pathway in **5** *vs* two in **4**, and/or to the flexibility-allowed non planarity of the DBA core. To bring light on this point, efforts have been devoted to the synthesis of the dianilinyl-*carbo*-cyclohexadiene **6** having a unique conduction pathway, as **5**, but locked in a rigid macrocycle as in **4** (**Figure 1**).



Scheme 1. Synthesis of *carbo*-cyclohexadienes **1** and **1F** from [6]pericyclynic precursors **2** and **2F** respectively [1,5]. An = 4-C_6H_4-OMe

The synthetic strategies previously developed for the preparation of related bis-trifluoromethylated *carbo*-cyclohexadienes [1,5] proved however not applicable to the preparation of **6**. Recent progress calling for alternative strategies towards this challenging target are reported hereafter.

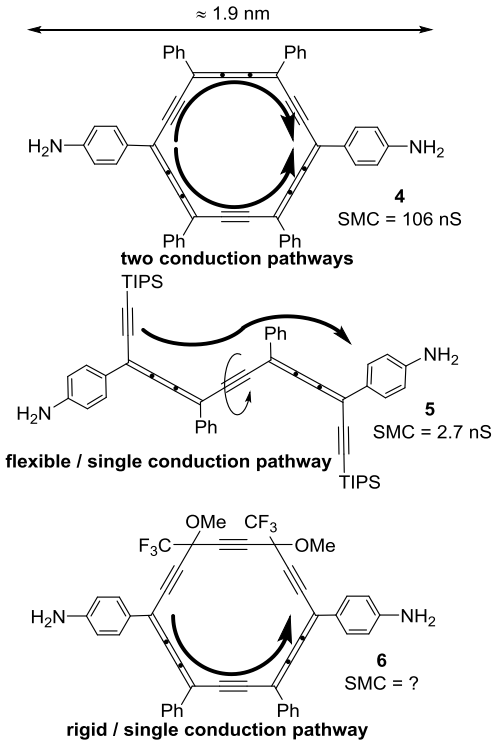
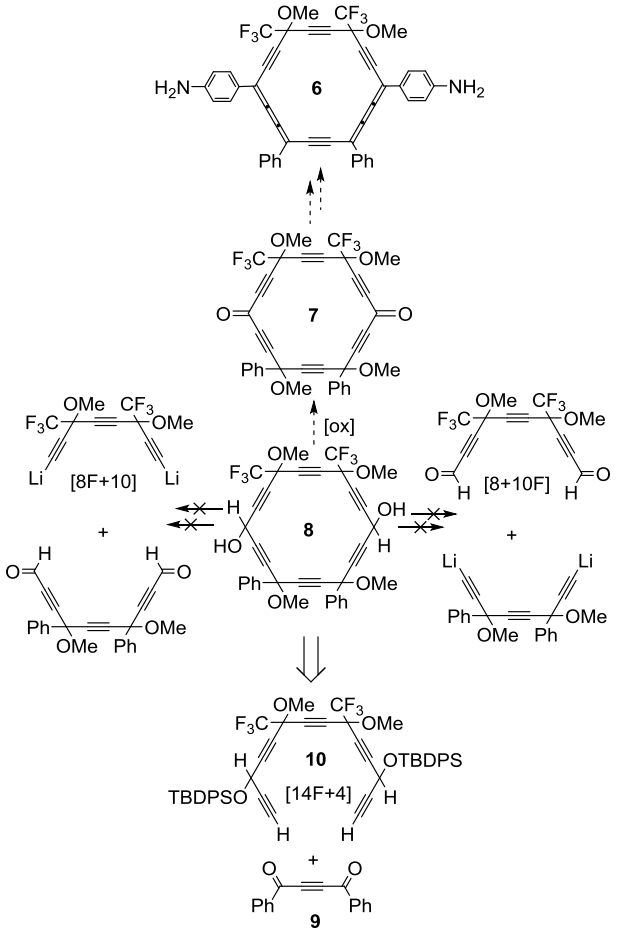


Figure 1. Dianilinyl-substituted DBA derivatives for SMC.

Results and discussion

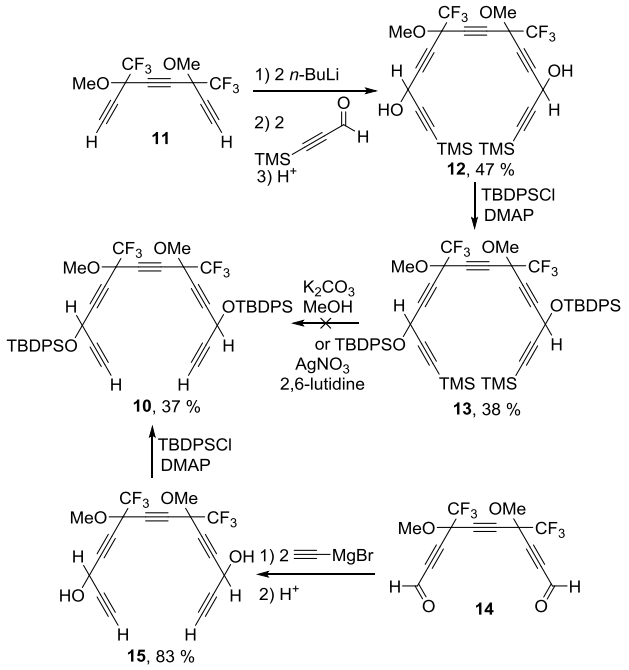
In a previous report on the preparation of the dianilinyl-*carbo*-benzene **4** and *carbo*-butadiene **5**, it has been evidenced that the aminophenyl substituents have to be anchored to the DBA core in a late stage because of the poor stability of the intermediates bearing anilinyl functions, even protected with trimethylsilyl groups [4g]. Therefore, the [6]pericyclynedione precursor **7** should be reacted with the protected anilinyl substituents at the last step, just before the final reduction to the *carbo*-cyclohexadiene **6**. First attempts at

preparing the diketone **7** through the use of either a [8F+10] or a [8+10F] macrocyclization procedure from a C_8 triyne and a C_{10} dialdehyde however failed to produce the targeted bis-secondary [6]pericyclynediol precursor **8** [5] (**Scheme 2**). Since the same approach had proved to be efficient for the preparation of the perphenylated analog of **7**, the failure of this method in the bis-trifluoromethylated series can be imputed to the effect of the CF_3 groups on the reactivity of the C_8 and C_{10} reactants.



Scheme 2. Envisaged synthetic approaches to the [6]pericyclynedione **7**, precursor of the bis-trirfluoromethylated *carbo*-cyclohexadiene **6**.

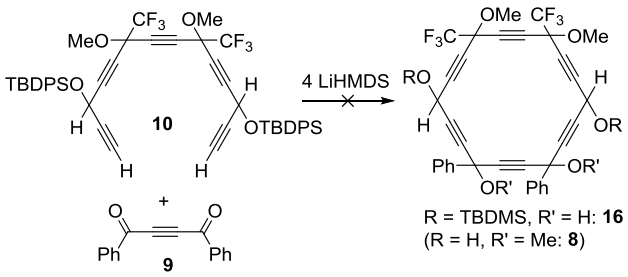
An alternative [14F+4] macrocyclization strategy was thus envisaged from the C_4 dibenzoylacetylene **9** [10] and the C_{14} bis-trifluoromethylated pentayne **10**. The synthesis of the latter was first attempted from the known triyne **11** [5] (**Scheme 3**). The first step consisted in the addition of the dilithium salt of **11** to two equivalents of trimethylsilylpropynal, itself prepared by a known procedure from lithium trimethylsilylacetylide and DMF [4f, 11]. In spite of a moderate stability, the bis-secondary diol product **12** was isolated in 47 % yield. Protection of the two OH groups with silyl substituents was then achieved by treatment of **12** with TBDPSCl and DMAP, giving **13** in 38 % yield. Attempt at selective desilylation of the two alkyne termini of **13**, using either K_2CO_3 in methanol, or $AgNO_3$/lutidine afforded undetermined polymeric materials only, instead of **10**.



Scheme 3. Synthesis of the C_{14} pentayne unit **10** for the proposed [14F+4] access to the [6]pericyclynediol **8** (**Scheme 2**).

An alternative method was then envisaged from the known dialdehyde **14**, prepared in two steps from the triyne **11** [5] (**Scheme 3**). The bis-terminal-pentaynediol **15** was first prepared in 84 % yield by treatment of **14** with ethynylmagnesium bromide. The targeted O-protected C_{14} pentayne **10** was then obtained in 37 % yield by treatment of **15** with TDBPSCl and DMAP.

A preliminary attempt at macrocyclization performed between the dilithium salt of the C_{14} precursor **10** and the C_4 diketone **9** provided an intractable polymeric mixture instead of the [6]pericyclynediol target **16** (**Scheme 4**). This result can be attributed to the high sensitivity of the lithiated intermediates. Working at lower temperature and over shorter reaction times should prevent polymerization and allow the isolation of **16**, precursor of the pericyclynediol target **8** and ultimately of the key diketone **7**.



Scheme 4. First attempt at [14F+4] macrocyclization for the preparation of the [6]pericyclynediol **16**.

Conclusions

As an alternative to the presently unproductive [8+10] cyclization strategy towards the [6]pericyclynediol **8**, putative precursor of the *p*-dianilinyl-*carbo*-cyclohexadienic conductor **6**, the [14F+4] strategy, unprecedented in the fluorinated series, can now be reasonably envisaged from the C_{14} bis-terminal pentayne **10** and the C_4 dibenzoylacetylene **9** (**Scheme 4**). Improvements of the experimental conditions are currently being sought to achieve the challenging synthesis of the *carbo*-cyclohexadiene **6** in view of the measurement of its SMC by STM-BJ.

Experimental section

General remarks. THF and diethyl ether were dried and distilled over sodium/benzophenone, dichloromethane (DCM) and pentane over calcium hydride. All others reagents were used as commercially available. Solutions of *n*-butyllithium were 2.5 M in hexane. All reactions were carried out under argon atmosphere, using Schlenk and vacuum line techniques. Column chromatography were carried out on silica gel (60 Å, C.C 70-200 μm). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used, ^{1}H and ^{13}C NMR: Brüker Avance 300 and Avance 400 spectrometers; mass spectroscopy: Quadrupolar Nermag R10-10H spectrometer; IR: Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR chemical shifts are in ppm with positive values

to high frequency relative to the tetramethylsilane reference for ^{1}H and ^{13}C, and CCl_3F reference for ^{19}F. Coupling constants *J* are in Hertz. Previously described procedures were used for the preparation of **9** [11], **11** [5] and **14** [5].

Experimental procedures and characterizations.

10. To a solution of **15** (0.10 g, 0.246 mmol) in dry DCM (10 mL) under stirring at r.t. were added first DMAP (0.075 g, 0.616 mmol), then ClTBDPS (0.17 g, 0.616 mmol). After stirring for 3 h at r.t., the mixture was treated with a saturated aqueous NH_4Cl solution. The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The brown residue was purified by silicagel chromatography (pentane:acetone 95:5) to give **10** as a pale brown oil in 37 % yield (0.080 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.11 (s, 18H, SiC(CH_3)$_3$), 2.53 (s, 2H, ≡C-*H*), 3.51 (s, 6H, OCH_3), 5.15 (s, 2H, C*H*OSi), 7.38-7.48 (m, 12H, *m*- and *p*-C_6H_5), 7.72-7.77 (m, 8H, *o*-C_6H_5). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -79.16, -79.19 (CF_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 19.2 (Si*C*(CH_3)$_3$), 26.5 (SiC(CH_3)$_3$), 53.6 (OCH_3), 54.0 (*C*HOSi), 70.7 (q, *J* = 35 Hz, *C*-CF_3), 73.2 (≡*C*-H), 73.3, 78.4, 79.7, 86.1 (*C*≡*C*), 121.11 (q, *J* = 283 Hz, *C*F_3), 127.8, 127.9 (2s, *o*- or *m*-C_6H_5), 130.1, 130.2 (*p*-C_6H_5), 131.9, 132.1 (2s, *i*-C_6H_5), 135.7 (*o*- or *m*-C_6H_5). MS (DCI/NH_3): *m/z*: 900.3 $[M+NH_4]^+$. FT-IR: ν: 1859-2960 (C-H Ar), 2127 (≡C-H), 1186 (C-O).

12. To a solution of the triyne **11** (0.240 g, 0.805 mmol) in dry THF (10 mL) under stirring at – 78 °C was added *n*-BuLi (0.74 mL, 1.85 mmol). The resulting mixture was stirred for 10 min at – 78 °C, then 1 h at r.t. before cooling back to – 78 °C. Then, a solution of trimethylsilylpropynal (0.250 g, 2.00 mmol) in dry THF (5 mL) was added, and the mixture was kept under stirring at – 78 °C for 4 h before treatment with a saturated aqueous NH_4Cl. The aqueous layer was extracted with diethylether, and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. The brown residue was purified by silicagel chromatography (Pentane:acetone 9:1), giving **12** as a pale brown oil in 47 % yield (0.208 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.22 (s, 18H, SiCH_3), 2.60 (bs, 2H, O*H*), 3.60 (s, 6H, OCH_3), 5.20 (bs, 2H, C*H*OH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -79.19-(-79.22) (CF_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = -0.5 (Si*C*H_3), 52.3 (O*C*H_3), 54.0 (*C*HOH), 70.72 (q, *J* = 36 Hz, *C*-CF_3), 73.6, 78.5, 85.9, 91.2, 100.0 (*C*≡*C*), 121.1 (q, *J* = 283 Hz, *C*F_3). MS (DCI/NH_3): *m/z*: 568.1 $[M+NH_4]^+$. HRMS (DCI/CH_4): *m/z* calcd for $C_{24}H_{27}O_3F_6Si_2$ $[M-H_2O+H]^+$: 533.1403, found: 533.1386. FT-IR: ν: 3395 (O-H), 2961 (C-H OMe), 2177 (C≡C), 1185 (C-O).

13. To a solution of **12** (0.140 g, 0.254 mmol) in dry DCM (10 mL) under stirring at r.t. were added DMAP (0.08 g, 0.636 mmol), and then ClTBDPS (0.18 g, 0.636 mmol). After stirring overnight at r.t., the mixture was treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The brown residue was purified by silicagel chromatography (pentane:DCM 9:1 then 7:3) giving **13** as a pale brown oil in 38 % yield (0.10 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.19 (2s, 18H, SiCH_3), 1.13 (2s, 18H, SiC(CH_3)$_3$), 3.55 (2s, 6H, OCH_3), 5.19 (2s, 2H, CHOSi), 7.42-7.50 (m, 12H, *m*- and *p*-C$_6H_5$), 7.76-7.84 (m, 8H, *o*-C$_6H_5$).

^{19}F NMR ($CDCl_3$, 376 MHz): δ = -79.10-(-79.20) (CF_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = -0.5 (SiCH$_3$), 19.3 (SiC(CH$_3$)$_3$), 26.5 (SiC(CH$_3$)$_3$), 53.9 (CHOSi), 54.2 (OCH$_3$), 70.8 (q, J = 36 Hz, C-CF$_3$)), 73.0, 78.4, 86.4, 90.4, 100.7 (C≡C), 121.2 (J = 284 Hz, CF$_3$), 127.7, 127.8 (2s, *o*- or *m*-C_6H_5), 130.0, 130.2 (2s, *p*-C_6H_5), 132.2, 132.4 (2s, *i*-C_6H_5), 135.7, 135.8 (2s, *o*- or *m*-C_6H_5). MS (DCI/NH_3): *m/z*: 1044.2 $[M+NH_4]^+$. FT-IR: ν: 2859-2960 (C-H Ar), 2127 (C≡C), 1185 (C-O).

15. To a solution of the dialdehyde **14** (0.21 g, 0.59 mmol) in dry Et_2O (20 mL) under stirring at 0 °C was added ethynylmagnesium bromide (3.56 mL, 1.78 mmol). The stirring was maintained for 15 min at 0 °C, then 3 h at r.t. before treatment with saturated aqueous NH_4Cl. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. The residue was purified by silicagel chromatography (pentane:acetone 7:3), giving **15** as a pale brown oil in 83 % yield (0.29 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.40 (bs, 2H, OH), 2.65 (s, 2H, ≡C-H), 3.60 (s, 6H, OCH_3), 5.24 (bs, 2H, CHOH). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -79.15, -79.16 (CF_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 51.6 (OCH$_3$), 54.1 (CHOH), 70.6 (q, J = 36 Hz, C-CF$_3$), 74.0 (≡C-H), 73.8, 78.6, 79.1, 85.5 (C≡C), 121.0 (q, J = 283 Hz, CF$_3$). MS (DCI/NH_3): *m/z*: 424.1 $[M+NH_4]^+$. FT-IR: ν: 3303 (O-H), 2127 (≡C-H), 1181 (C-O).

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