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Synthesis of bent [4]phenylene (cyclobuta[1,2-*a*:3,4-b′]bisbiphenylene) and structure of a bis(trimethylsilyl) derivative: the last [4]phenylene isomer†

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The syntheses of the title compounds were accomplished by cobalt-catalyzed alkyne cyclotrimerizations using two strategies; the properties of the bent phenylene frame reflect the combined effects of benzocyclobutadienofusion of the component [3]phenylene substructures.

Among the simple phenylene topologies hitherto assembled—linear, angular, zig-zag, and branched[1]—is a glaring omission, bent [4]phenylene **1**. This compound is of interest because it constitutes the fifth and last [4]phenylene isomer,[2] and its preparation allows the completion of an experimental analysis of the comparative properties of this group of topomers, including data based on calculations.[3] Hydrocarbon **1** is also the first and smallest member of a subclass of phenylenes in which the linear and angular topologies are juxtaposed. Infinite arrays of either (but not mixed) type have been analyzed theoretically as potential novel electronic and magnetic materials.[4]

It is instructive to view **1** as the result of benzocyclobutadienofusion of **2** and **3**, respectively (Fig. 1). Such alteration of **2** is expected to cause increased bond alternation in ring C, relieving the antiaromaticity of the neighboring cyclobutadiene fragment, in turn 'relaxing' the bisallyl frame of B to become more benzenoid, *i.e.* diatropic and perhaps *less* reactive. In turn, the effect of the corresponding fusion on **3** is anticipated to be bond alternation in ring B in the direction indicated in structure **1** and thus, by relay, even more pronounced cylohexatriene character[6] in C, rendering this ring even less diatropic and possibly *more* reactive. One notes (Fig. 1) that the trends in NICS values[3a] corroborate these expectations. Does this simple picture hold?

Scheme 1 depicts the strategy used to assemble **1**, starting with 2,3-diiodobiphenylene[7] and its (non-selective) Pd-catalyzed coupling with a protected *o*-diethynylbenzene synthon **5**[1a,d] to give **6**. Subsequent (trimethylsilyl)ethynylation and deprotection furnished triyne **7**, which underwent cobalt-catalyzed cyclization to give orange, air-sensitive **1** in 8 steps (from *o*-diethynylbenzene) and 1.7% overall yield.[8] A more convergent double cyclization approach is depicted in Scheme 2 and features the remarkably regioselective desymmetrization of 1,2,4,5-tetrabromobenzene to the 5-iodotribromo analogue, allowing for its selective alkynylation to eventually furnish pentayne **8**.[9] Simultaneous intra- and intermolecular [2 + 2 + 2]cycloaddition in bis(trimethylsilyl)acetylene produced the relatively (with respect to **1**) less sensitive **9** in 5 steps and 7% overall yield.[8] While this derivative decomposed on attempted conversion to **1**, it proved valuable as a source of material suitable for X-ray crystal analysis (Fig. 2)[10] and preliminary experiments.

On the basis of the NMR criterion of aromaticity,[11] the answer to the above question is affirmative. Thus (Fig. 1), the protons of ring C in **1** are shielded relative to those corresponding in **3** (and **4**), and H6 more so than H5. On the other hand, the

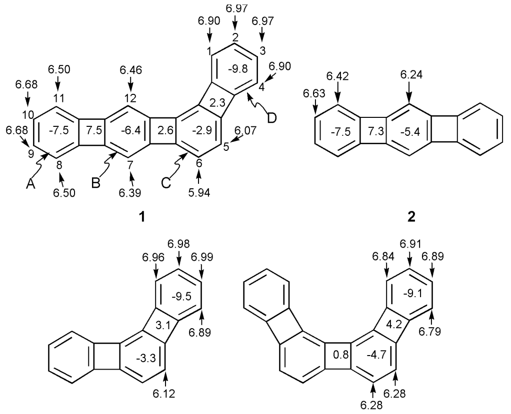
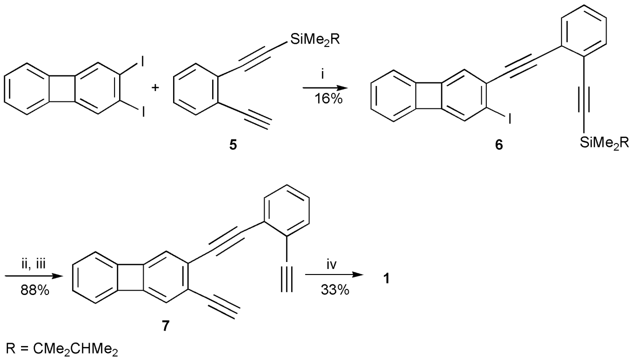
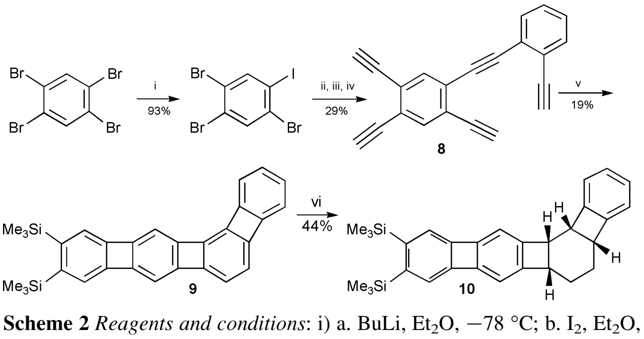


Fig. 1 ^{1}H NMR chemical shifts (CDCl$_3$, δ, ppm) and NICS values (inside the respective rings) of **1–4,** and labeling of the benzene rings in **1** (A–D).



Scheme 1 *Reagents and conditions*: i) [Pd(MeCN)$_2$Cl$_2$], CuI, PPh$_3$, piperidine, 90 °C, 40 h. ii) Me$_3$SiC$_2$H, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, piperidine, 44 h. iii) Bu$_4$NF, THF, 20 min. iv) CpCo(CO)$_2$, *m*-xylene, h*ν*, Δ, 15 h.



Scheme 2 *Reagents and conditions*: i) a. BuLi, Et$_2$O, −78 °C; b. I$_2$, Et$_2$O, −78 °C. ii) **5**, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, Et$_3$N, 15 h. iii) Me$_3$SiC$_2$H, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, Et$_3$N, 120 °C, 2.5 d. iv) Bu$_4$NF, THF, 2 h. v) CpCo(CO)$_2$, Me$_3$SiC$_2$SiMe$_3$, h*ν*, Δ, 16 h. vi) H$_2$, 1 atm, Pd/C, Et$_2$O, 10 min.

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† Electronic supplementary information (ESI) available: selected bond distances and angles for **9**, spectral and analytical information. See http://www.rsc.org/suppdata/cc/b1/b109789j/

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protons of ring B are deshielded compared to those corresponding in **2**, the slightly larger chemical shift of H12 being typical of 'bay region' hydrogens in the phenylenes.[1a] The most notable effect in the ^{13}C NMR spectra is the shielding ($\sim$2–6 ppm) of the carbons of ring C relative to those corresponding in **3** (and **4**), again signalling increased cyclohexatrienic character.[1]

The calculated (HF/6-31G*)[3b] energies (kcal mol^{-1}) within the series of [4]phenylene isomers decrease with the number of angular fusions in the order linear (relative energy +11.0) > **1** (+5.9) > **4** (+4.5) = zigzag (+4.3) > C_3-symmetric [4]phenylene (0). Comparison of the ^{1}H NMR data[1a,d] reveals that this trend is (roughly) paralleled by net increased deshielding of all the hydrogens (δ_{average} = 6.33, 6.58, 6.70, 6.66, 7.19, respectively), as expected on the basis of GIAO and NICS calculations[3b] which predict overall decreasing paratropic and correspondingly increasing diatropic character of the cyclobutadiene and benzene rings, respectively. Interestingly, in as much as these trends may be reflected in increasing HOMO–LUMO gaps along the series and, in turn, in the electronic spectra, **1** displays a lowest energy λ_{max} at 486 nm, almost identical to that of the topomeric linear framework (λ_{max} at 488 nm), whereas the other isomers show relative hypsochromic shifts.[1a,d] It appears that the presence of linear substructures has a strong effect on the phenylene chromophore, as observed previously in the branched series.[1b]

The crystal structure of **9** reveals the distinctive patterns of bond length and angle distortions observed for the substructures **2** and **3** (identical within the range of standard deviations),[5] particularly for rings C and D. Not surprisingly,[12] the subtle effects of the added ring fusion on the remote benzene rings are not clearly evident. Quite noticeable, however, is the curvature of **9**,[5a] rendering the molecule chiral. The dihedral angles between the planes of fused rings range from 1.32–6.38°, and the displacements of other ring carbons from the mean plane defined by those of ring D range from 0.07 to 1.70 Å.

On the basis of the respective ease of all-*cis*-hexahydrogenation of **2** (H_2, 1 atm, Pd/C)[7] and **3** (H_2, 15 atm, Pd/C),[1a] the central ring in the former may be regarded to be more activated than that in the latter. In **1**, ring B was expected to be relatively stabilized, ring C destabilized, the relative extent of which was tested on **9**. Thus, **9** underwent smooth hydrogenation (Scheme 2) under mild conditions to furnish **10** completely regioselectively,[8] indicating a complete reversal in relative reactivity of the inside six-membered rings. Proof of the structure of **10** rests on spectral data, especially low temperature ^{1}H NMR spectra which allowed the detection of two distinct, interconverting conformers (1 : 1)[13] containing diagnostic doublets assignable to H7, H8, H11, and H12.

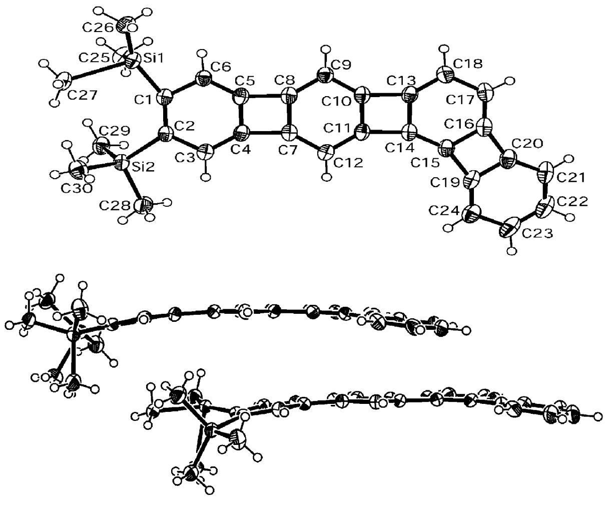

Fig. 2 Structure of **9** in the crystal: views from above (top) and the side (bottom). For selected distances (Å) and angles (°), see ESI†

In summary, the synthesis of the last isomer of the [4]phenylenes has been accomplished. Its properties constitute a blend of those of the component linear and angular [3]phenylene substructures, and further delineate the effect of topology on the interplay between antiaromatic cyclobutadienoid and aromatic cyclohexatrienic-benzenoid circuits.

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8 For spectral and analytical data of **1**, **9**, and **10**, see ESI†.

9 An alternative construction of **8**, starting from 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene (ref. 7), and its desymmetrization by monodesilylation (CH_3Li), or from 1,2,4,5-tetraethynylbenzene and respective single Pd-catalyzed couplings to *o*-iodo(trimethylsilylethynyl)benzene proceeded in only statistical fashion.

10 *Crystal data.* $C_{30}H_{28}Si_2$, M 444.72, monoclinic, a = 9.5453 (2), b = 22.1287 (3), c = 12.0525 (1) Å, β = 103.155 (1)°, V = 2478.99 (9) Å^3, T = 147 K, space group $P2_1$ (#4), Z = 4, μ (Mo-K$_\alpha$) 1.58 cm^{-1}, 10629 reflections measured, 7220 unique reflections [$I > 3.00\sigma(I)$, R_{int} = 0.027] were used in refinement. The final $wR(F)$ was 0.040 (all data). CCDC 173172. See http://www.rsc.org/suppdata/cc/b1/b109789j/ for crystallographic files in .cif or other electronic format.

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