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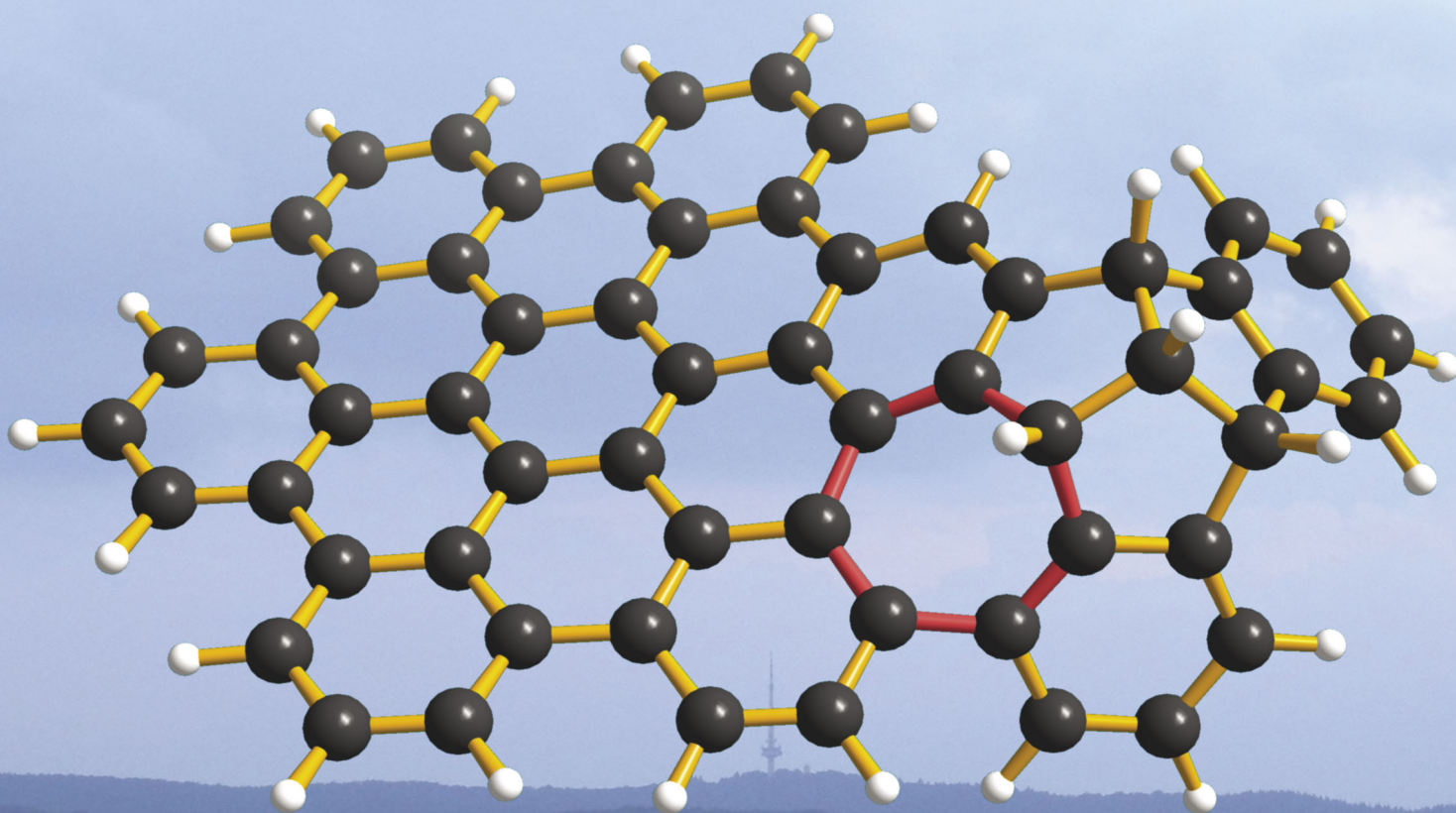
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COMMUNICATION
Ehsan Ullah Mughal and Dietmar Kuck
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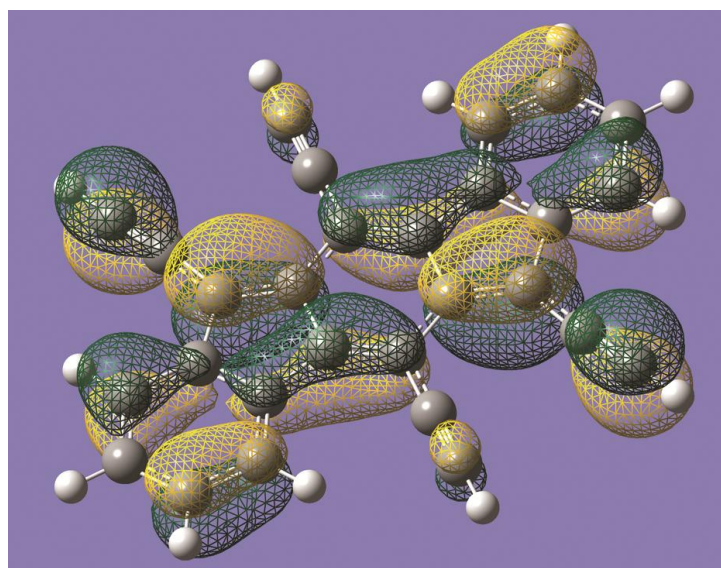a cycloheptatriene unit generated by Scholl reaction

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Merging tribenzotriquinacene with hexa-*peri*-hexabenzocoronene: a cycloheptatriene unit generated by Scholl reaction†‡
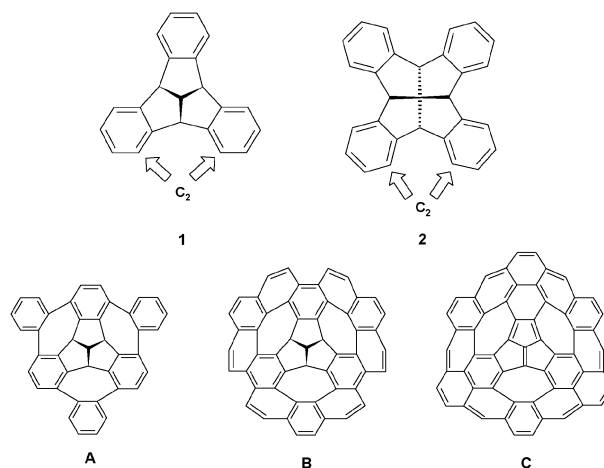
Ehsan Ullah Mughal and Dietmar Kuck*

The single-wing extension of the bowl-shaped tribenzotriquinacene (TBTQ) framework with polycondensed aromatic hydrocarbon units has been reported. In the course of a Scholl reaction, one of the three-dimensional bays of the TBTQ core has been bridged by a PAH unit to generate a seven-membered ring within the merged TBTQ-(hexa-*peri*-hexabenzocoronene) scaffold.

The construction and properties of carbon networks containing extended conjugated π-electron systems have fascinated chemists for a long time.[1–4] Along with the improved access of the curved polycyclic hydrocarbons such as corannulene, its derivatives[5–7] and congeners, such as other [*n*]circulenes,[8,9] and the advent of the fullerenes and nanotubes,[10] the directed synthetic construction of carbon-rich scaffolds as promising nanoscale electronic materials has enjoyed a strong revival of scientific efforts.[11] Some members of the centropolyindane hydrocarbons[12] also appertain to such structural motifs. In particular, as shown recently,[12c,13] the polycyclic core structure of tribenzotriquinacene (TBTQ, **1**)[12,14,15] offers interesting possibilities to enforce the construction of bowl-shaped poly-condensed aromatic networks.[16] This is due to the fact that, from a geometrical point of view, the three three-dimensional bays of the TBTQ skeleton are perfectly suited for incorporating C₂-bridges, such as 1,2-vinylene or 1,2-benzeno units, between the pairwise opposite *ortho* positions. A similar geometrical argument holds true for the four 3-D bays of the saddle-shaped framework of fenestrindane (**2**).[12c,17] Tribenzotri-quinacene and its derivatives are readily accessible;[12–16,18–20] therefore, the TBTQ framework appears to be particularly promising to construct graphene-like architectures bearing a saturated bowl-shaped centre, such as in **A** and **B**, or even the fully unsaturated tribenzoacepentalene core,[21] such as in **C** (Fig. 1). Euler's polyhedron formula, discovered 260 years ago, may be recalled here since it allows us to predict that

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‡ Electronic supplementary information (ESI) available: Calculated structures of compound **10**; experimental procedures, spectroscopic data and ¹H and ¹³C NMR spectra of all new compounds; ¹H,¹H-COSY spectra, MALDI mass spectra and UV/vis and luminescence spectra of compounds **8** and **10**. See DOI: 10.1039/c2cc34245f

Fig. 1 Bowl-shaped tribenzotriquinacene (**1**) and hypothetical poly-condensed aromatic congeners bearing three bridging 1,2-benzeno units (**A**), a full belt-like sphere (**B**) and the fully unsaturated acepen-talene core (**C**). Also shown is fenestrindane (**2**), a saddle-shaped analogue of **1**.

seven-membered rings compensate for the out-of-plane bending effect of five-membered rings in graphs consisting exclusively of trivalent vertices.[22]

Whereas threefold embedding of the TBTQ core to TBTQ-centred graphene cuttings is most challenging and corresponds to an exhaustive (twelvefold) functionalisation of the TBTQ molecular periphery, directed extension of only one of the three wings of the TBTQ framework may be more readily achievable[23] and help to pave the way to the threefold scaffolds as the ultimate goals.[12c,13,16] In this contribution, we present our first results of a study aimed at the synthesis of a tribenzotriquinacene containing a single PAH unit bridging one of the 3-D bays of the TBTQ core. As will be shown, we succeeded for the first time in generating a cycloheptatriene ring fused to the mutually merged frameworks of both the bowl-shaped TBTQ and a (quasi-planar) hexa-*peri*-hexabenzocoronene.
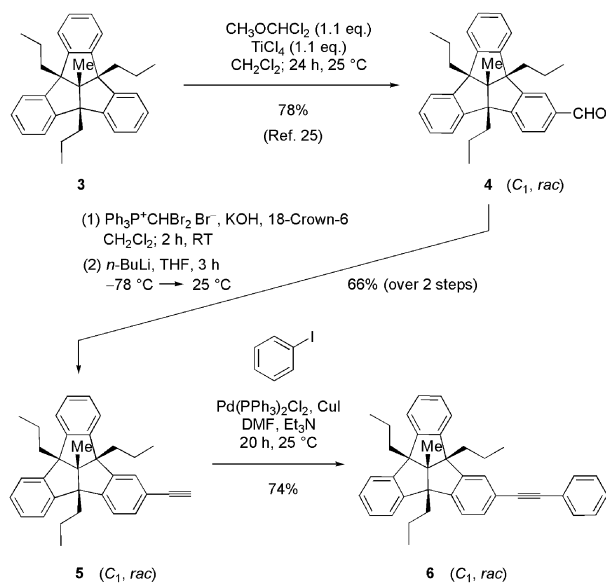
4*b*,8*b*,12*b*-Tri-*n*-propyl-12*d*-methyltribenzotriquinacene **3**[24,25] was used as the starting material since we hoped that the elongated bridgehead alkyl groups would help to avoid solu-bility problems (Scheme 1).[24] Single functionalisation at the outer periphery was performed by formylation giving the corresponding TBTQ aldehyde **4**, as described recently,[25]

Scheme 1 Synthesis of TBTQ-based acetylenes **5** and **6**.

and this product was converted into the hitherto unknown ethynyl derivative **5** by a modified Corey–Fuchs procedure in 66% overall yield.[26] The intermediate obtained from **4** and dibromomethyltriphenylphosphonium bromide[27] under PTC conditions was purified but not completely characterised. Various attempts by using classical conditions ($PPh_3/Zn/CBr_4$ in the first step)[28] for the conversion **4** → **5** failed. Subsequent Pd(0)-catalysed Sonogashira–Hagihara reaction of the simple TBTQ monoacetylene **5** with iodobenzene furnished the corresponding tolane analogue **6** in good yield. Even better yields (74%) were obtained when the reaction was carried out in DMF–triethylamine mixtures instead of THF–piperidine.[29] Both TBTQ acetylenes, **5** and **6**, were condensed with tetra-phenylcyclopentadienone (tetracyclone) in diphenyl ether at 250 °C to afford the tetraphenylphenyl- and pentaphenylphenyl-TBTQ derivatives **7** and **9**, respectively, in high yields (Scheme 2).[30] Hydrocarbons **7** and **9** were characterised by ^{1}H and ^{13}C NMR spectroscopy and by mass spectrometry; however, in spite of the good solubility of these compounds, some of their ^{1}H resonances were not clearly resolved even at high (100 °C) or low temperatures (−50 °C) due to the particularly strong crowding caused by the TBTQ core.

The final cyclodehydrogenation of the oligophenylphenyl-TBTQ derivatives **7** and **9** was performed under Lewis-acidic conditions.[31] Different oxidant systems including $Cu(CF_3SO_3)_2$–$AlCl_3$–CS_2[32] and $FeCl_3$–$MeNO_2$–CH_2Cl_2,[33] at 25 °C in both cases, were attempted. Use of $FeCl_3$ gave only the starting materials. Best results were obtained by using the $Cu(CF_3SO_3)_2$–$AlCl_3$–CS_2 system at 40–45 °C;[34] side reactions such as dealkyl-ation, chlorination,[35] or migration of alkyl substituents[36] were not observed. Cyclodehydrogenation proceeded smoothly and exclusively in an intramolecular fashion[33] to afford the poly-condensed TBTQ derivatives **8** and **10**, respectively, in good yields. Products of incomplete cyclisation were not observed.

The polycondensed TBTQ compounds **8** and **10** were charac-terized by various spectroscopic methods including matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and UV/vis
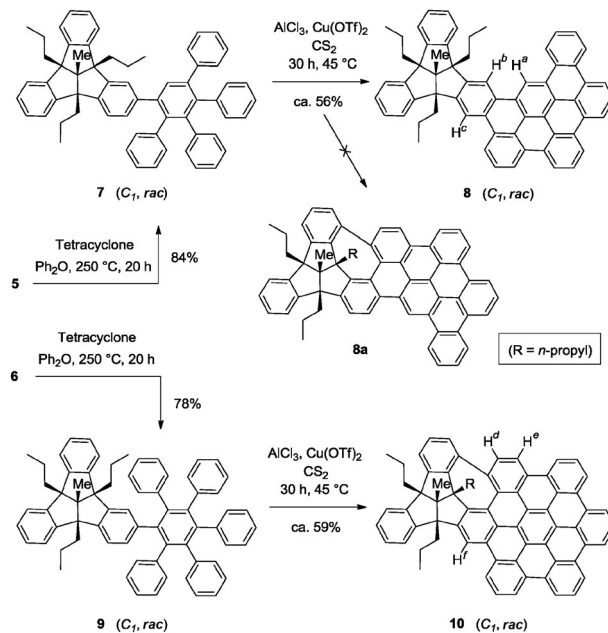
Scheme 2 Synthesis of oligophenylphenyl-TBTQ derivatives **7** and **9** and subsequent Scholl reaction leading to the condensed TBTQ hydrocarbons **8** and **10**, respectively. Note that the bay-bridging twofold cyclodehydrogenation giving the cycloheptatriene unit in the case of **10** does not occur with the lower analogue **7**.

spectroscopy. The lowest-energy absorption of **8** was found at λ_{max} = 376 nm and that of **10** at λ_{max} = 415 nm.[37] ^{1}H NMR chemical shifts were recorded in 1,1,2,2-tetrachloroethane-d_2 at different temperatures (23 °C and 110 °C). At ambient temperature, signal broadening was found in both cases, suggesting strong intermolecular association by π-stacking interaction.[38] Sharp signals were obtained at 110 °C, thus indicating a decrease of intermolecular aggregation at higher temperatures.[39] While complete site-specific assignment of the protons in **8** and **10** was not achieved, unequivocal identifi-cation of the hydrocarbons was deduced from a number of independent features. In the case of hydrocarbon **8**, the MALDI-TOF mass spectrum proved fourfold cyclodehydro-genation by a clean $M^{+\cdot}$ ion cluster having its nominal peak at m/z 792, as expected. The ^{1}H NMR spectrum exhibits a characteristic singlet resonance for the doubly bay-sited proton (H^a) at extremely low field (δ 9.91) as well as two further low-field singlets at δ 8.90 and 8.74 for H^b and H^c. The residual arene resonances and the aliphatic ^{1}H resonances also corroborate the structure of **8**. For example, due to its C_1-molecular symmetry, the propyl resonances of **8** suffer characteristic splitting. Notably, both the MALDI and the ^{1}H NMR spectra reveal that the other expected product of sixfold cyclodehydrogenation, **8a** (Scheme 2), did not form to a significant extent (see below). In particular, the peak at m/z 790 may indicate that the molecular ion of **8a** amounts to ≤2% of that at m/z 792 for ion **8**$^{+\bullet}$. Hydrocarbon **10** revealed pronounced concentration and temperature dependence of the ^{1}H resonances, in line with general experience on hexa-peri-hexabenzocoronenes.[40] Nevertheless, unequivocal spectroscopic

features corroborate the identity of **10** as well. The ^{1}H NMR spectrum recorded at 110 °C exhibits a diagnostic singlet at δ 9.25 for H^f, the only isolated proton of the molecular structure, and two doublets at even lower field (δ 9.41 and 9.32). The former resonance is attributed to H^d as a part of an AB spin system with H^e ($\delta \approx$ 8.72), as confirmed by ^{1}H,^{1}H-COSY spectroscopy at elevated temperatures, again in line with the structure of **10**. Moreover, MALDI-TOF mass spectrometry indicates the sevenfold cyclodehydrogenation of the precursor **9**.

The nominal-mass peak of hydrocarbon **10** appeared at m/z 862 and the observed isotopic pattern was in good agreement with the theoretical distribution. Further features of the ^{1}H and ^{13}C NMR spectra unequivocally confirm the structure of **10** and thus, in this case, the formation of a seven-membered ring fused into the curved polycyclic framework of the TBTQ-merged hexa-*peri*-hexabenzocoronene **10**.

The efficient generation of a cycloheptatriene ring by incorporating a 1,2-benzeno unit between the *ortho*- and *ortho'* positions of one of the rigid diphenylmethane units of the TBTQ framework is a promising finding. It may broaden the use of the Scholl reaction for the construction of seven-membered rings[41,42] in polycondensed aromatic hydrocarbon networks, provided that this kind of twofold cyclodehydrogenation across the C$_5$-bays of the centropolyindanes **1** and **2** is structurally enforced.[43,44] Thus, access to novel bowl- and saddle-shaped graphene cuttings appears to be in reach.

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