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COMMUNICATION

Ortho-methylated tribenzotriquinacenes—paving the way to curved carbon networks†‡

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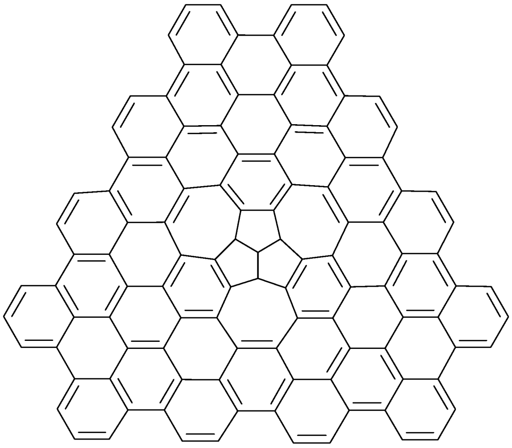
The synthesis of sterically crowded tribenzotriquinacenes with complete and partial methylation of the *ortho*-positions has been achieved using the double cyclodehydration strategy. This leads to a twisted tribenzotriquinacene core and enables further functionalization for the future synthesis of curved model compounds for defective carbon networks.

Graphene and its unique properties have recently spurred a huge increase in interest.[1] Not only electronic applications of as-grown graphene materials but also the controlled modification of their chemical and electronic properties by chemical functionalization have been discussed in detail.[2]

One of the major issues of its structure is the existence of lattice defects related to the insertion of non-hexagonal rings, *i.e.* pentagons and heptagons.[3] These do not only induce a local curvature, such as a bowl shaped indentation, in the otherwise flat network but also have a major impact on the electronic and magnetic properties of the material.[4] Kaiser *et al.* have recently published the direct imaging of such defects using STEM, showing the existence of fused pentagonal defects in pentalene-like structures as well as the existence of heptagons in the graphene lattice.[5] Furthermore, these defects play a role in the formation of new classes of two-dimensional materials such as amorphous sp^2 carbon.[6]

A model for non-aromatic bowl shaped defects in graphene including fused pentagons and heptagons has been proposed by Tellenbröker and Kuck.[7] The structure of a respective defective graphene flake would be derived from a suitably embedded tribenzotriquinacene (TBTQ) **2a** after its dehydrogenation (Fig. 1). It would be highly desirable to synthesize defined molecules such as **3** where the pre-shaped bays of the TBTQ core are bridged with 1,2-vinylidene units in order to study the resulting properties of such a "faulty graphene flake" fragment. However, the synthesis cannot be adapted from the formation of flat and defect-free nanographene fragments, which can be obtained using *e.g.* methods reported by Müllen and coworkers.[8] The synthesis of the model compound **3** has rather to be adapted from the stepwise formation of the tribenzotriquinacene unit as reported by Kuck[9] and requires inevitably the partial or complete substitution of the hydrogen atoms in the *ortho*-positions of the aromatic rings.



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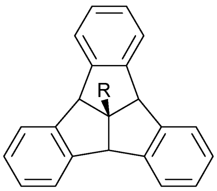

2 a: R = H
b: R = Me

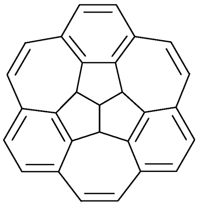

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Fig. 1 The structures of a defective carbon flake (**1**) and related model compounds (**2** and **3**).

However, in addition to the derivatization at the three bridgehead positions, so far only *meta*-substituted derivatives of **2** have been reported as sterical hindrance impedes the

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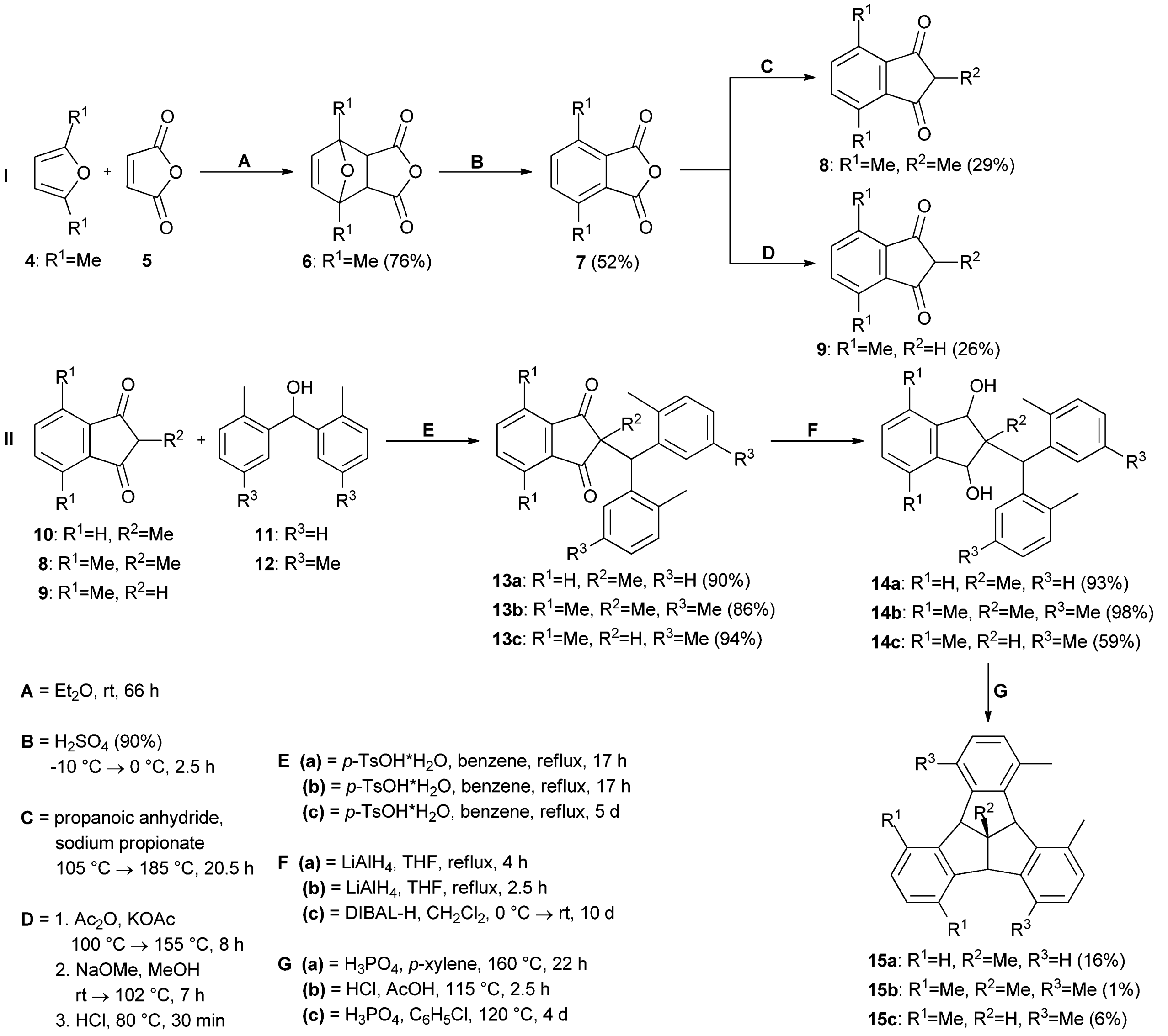
derivatization of the tribenzotriquinacene in the *ortho*-position by subsequent aromatic substitution.[7,10] Kuck discussed the challenging nature of the required transformations in 2006.[11] Here we describe the synthesis of such sterically crowded tribenzotriquinacenes carrying up to six methyl groups in the *ortho*-positions of the benzene rings based on the introduction of the methyl substituents at the beginning of the synthetic scheme.

Since it was expected that the level of steric hindrance is increasing with the number of methyl groups attached in the *ortho*-positions of the starting materials, the first synthetic attempt was made to insert only two methyl groups. Therefore, the originally reported synthesis of unsubstituted TBTQ **2**[12] had to be modified (Scheme 1). The required 1,3-indandione **10** and the dimethylated benzhydrol derivative **11** were prepared according to procedures described in the literature.[13] After their conversion to the corresponding 2-methyl-2-benzhydryl-1,3-indandione **13a** and subsequent reduction to the indandiol **14a** the final double cyclodehydration step was accomplished with H_3PO_4 in *p*-xylene at elevated temperature. Despite the sterical influence of the two additional methyl groups Me_3-TBTQ **15a** could be obtained in 16% yield. (The unsubstituted Me-TBTQ **2b** is obtained with 33% yield under comparable conditions.)[12]

The successful synthesis of Me_3-TBTQ **15a** shows the feasibility of the introduction of substituents in the *ortho*-positions at an early stage of the sequence. To extend this new access to entirely *ortho*-methylated TBTQs, the methylated indandiols **8** and **9** as well as the tetramethylated benzhydrol-derivative **12** were prepared according to literature procedures; starting with a Diels–Alder reaction of 2,5-dimethylfuran **4** and maleic anhydride **5**, followed by dehydration of adduct **6** to the phthalic anhydride **7** and subsequent conversions to **8** and **9**, respectively.[13b,14] The reaction of **8** and **9** with the benzhydrol-derivative **12** yielded the 2-benzhydryl-1,3-indandiones **13b** and **13c** which could be reduced to their corresponding 2-benzhydryl-1,3-indandiols **14b** and **14c**.



Scheme 1 Synthesis of tribenzotriquinacenes carrying up to six methyl groups in the *ortho*-positions of the aromatic rings using the cyclodehydration step as the structure-defining transformation.

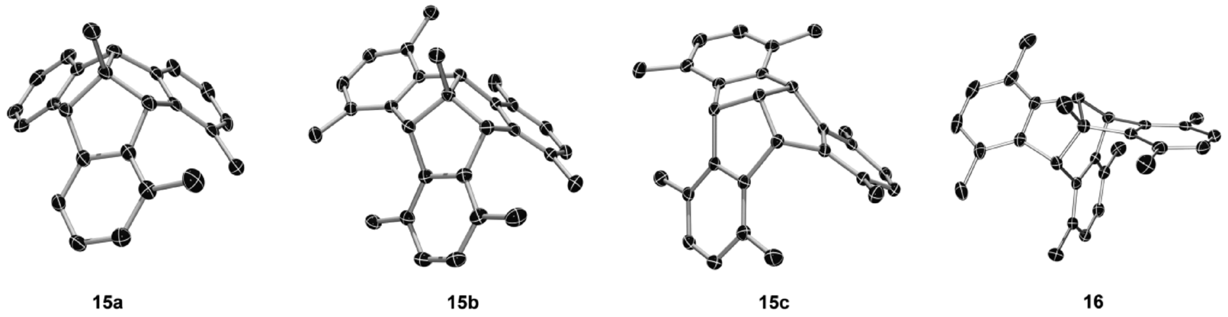

15a **15b** **15c** **16**

Fig. 2 X-Ray structures of *ortho*-substituted tribenzotriquinacenes **15a–c** and the rearrangement product **16**. In the crystal no molecular symmetry is observed due to steric repulsion of the adjacent methyl groups. In contrast, $^1H/^{13}C$ NMR spectra for **15a**, **15b** and **15c** in solution exhibit the typical signal patterns reflecting C_s- and C_{3v}-symmetries, respectively. Even at low-temperature (197.3 K) no line broadening or separation was observed.

The final double cyclodehydration step represents the challenge in this synthetic approach. All attempts to synthesize Me$_7$-TBTQ **15b** using a variety of conditions (*i.e.* H_3PO_4/chlorobenzene; H_3PO_4/xylene; $AlCl_3$/dichloromethane; Amberlyst 15/benzene; Amberlyte 120/toluene) were to no avail. In some cases (Amberlyst 15/benzene; $AlCl_3$/dichloromethane) the product of a Wagner–Meerwein rearrangement was isolated. In contrast, under strongly acidic conditions (HCl/HOAc), the desired Me$_7$-TBTQ **15b** was obtained in 1% yield besides the above-mentioned rearrangement product **16** (36%, see Fig. 2 for crystal structure). **16** results from the formation of a tertiary carbocation from the initially generated secondary benzylic carbocation (Scheme S1 in the ESI‡).[15]

In contrast, the driving force for such a rearrangement should be significantly reduced when the methyl group at the central carbon is missing. Therefore, the formation of Me$_6$-TBTQ **15c** should be less hampered by this concurrent reaction pathway.

Although attempts using a variety of dehydration conditions (*i.e.* Amberlyst 15/benzene; $AlCl_3$/dichloromethane; PPA/chlorobenzene) did not give the rearrangement product as expected, the Me$_6$-TBTQ **15c** was only found in traces at the maximum. Furthermore, the application of strongly acidic conditions (HCl/HOAc) afforded the product of an elimination–substitution sequence leading to a chlorinated indene moiety **17** (see ESI‡).

The successful synthesis of Me$_6$-TBTQ **15c** was achieved using H_3PO_4/chlorobenzene at 120 °C in the cyclodehydration step. Due to the reduced symmetry of the product (Fig. 2) the solubility of **15c** was markedly increased in comparison to the rigid and highly symmetrical unsubstituted **2a** and crystallization was not successful for the isolation of **15c** (as for the isolation of **15a** and **15b**). Only multistep chromatographic workup (column chromatography, HPLC/MPLC) provided the desired product in up to 6% yield,[16] which is surprisingly high regarding the maximum yield of 11% for the unsubstituted compound **2a**.[12]

In summary, the synthesis of three *ortho*-methylated tribenzotriquinacenes was achieved using the well-established cyclodehydration strategy with suitably substituted benzhydrylindane-1,3-diols. The further functionalization (*e.g.* oxidation and subsequent intramolecular coupling) of the title compounds and the synthesis of benzannulated derivatives of TBTQ will open the way to the formation of bridged tribenzotriquinacenes, which will be useful for the investigation of curved defects in graphene-derived structures and their effect on electronic properties of defective carbon networks.

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15 The synthesis of a similar structure as **16** with H/*t*-BuO/*t*-Bu residues instead of methyl groups has been reported by Okada *et al.* via a different reaction sequence in K. Okada, H. Kawai, K. Okubo, T. Uesugi and M. Oda, *Tetrahedron Lett.*, 1988, **29**, 2333.

16 Isolated yields vary between 3–6% depending on the scale of synthesis due to demanding isolation processes.