

# Quadrannulene: A Nonclassical Fullerene Fragment\*\*

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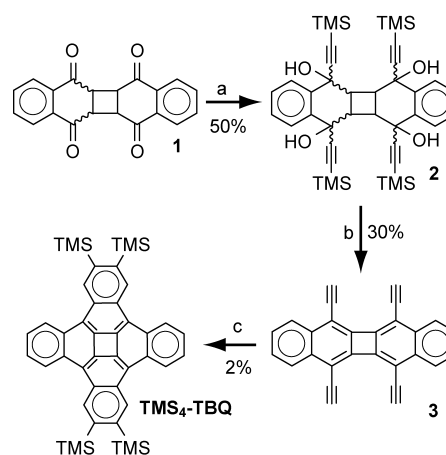
Dedicated to Professor Josef Michl

The presence of nonhexagonal rings in an otherwise graphitic lattice induces curvature. Pentagons are common—twelve pentagons surrounded by hexagons make up  $C_{60}$ . Larger rings are present in Stone–Wales defects, and the polyhedral formula of Euler mandates their existence in carbon nanotube Y-junctions.<sup>[1]</sup> Except for a single, partially saturated example,<sup>[2]</sup> four-membered rings in graphitic structures are, however, unknown. The smallest examples of these graphitic structures are the  $[n]$ circulenes, wherein a central  $n$ -sided polygon is surrounded by  $n$ -fused benzenoid rings.<sup>[3]</sup> [7]Circulene, first prepared by Yamamoto, Nakazaki, and co-workers in 1983, is saddle shaped.<sup>[4]</sup> [6]Circulene, or coronene, is the trivial, planar case, and it was first synthesized by Scholl and Meyer in 1932<sup>[5]</sup> but also occurs naturally. [5]Circulene, or corannulene, comprises 1/3 of the  $C_{60}$  skeleton and has been intensely studied,<sup>[6]</sup> and it was first prepared by Lawton and Barth in 1971.<sup>[7]</sup> Whereas a few pioneering attempts have been reported,<sup>[8]</sup> [4]circulene has never been synthesized before.

We report herein the preparation and characterization of a stable [4]circulene. By analogy with Lawton's naming of corannulene (Latin: *cor*, heart; *annula*, ring),<sup>[7]</sup> we suggest the trivial name quadrannulene (Latin: *quadra*, square; *annula*, ring) for the [4]circulene parent. Hence, we name this derivative 1,8,9,16-tetrakis(trimethylsilyl)tetra-*cata*-tetraben-

zoquadrannulene, abbreviated TMS<sub>4</sub>-TBQ. The IUPAC name and atom numbering are given in the Supporting Information.

Our unoptimized five-step synthesis (Scheme 1) provides TMS<sub>4</sub>-TBQ in very low yield. Hopf and co-workers recently summarized two synthetic strategies to the quadrannulene core:<sup>[8]</sup> making the four-membered ring from [2,2]-paracyclo-



**Scheme 1.** Synthesis of TMS<sub>4</sub>-TBQ. Reaction conditions: a) trimethylsilylacetylene, BuLi, CeCl<sub>3</sub>, THF, −78 °C to 25 °C; b) 1. TsOH, toluene, reflux, 2. KOH, MeOH, 25 °C; c) 1. CpCo(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>, bis(trimethylsilyl)acetylene, DME, 25 °C, 2. Cp<sub>2</sub>FePF<sub>6</sub>, DME = 1,2-dimethoxyethane, TMS = trimethylsilyl. Full experimental procedures can be found in the Supporting Information.

phanes (e.g., by aryne dimerization), or bridging substituents adjacent to the four-membered ring (positions 1,8 and 4,5) of a biphenylene core. We used the latter approach, which has the advantage that the strain associated with the four-membered ring is introduced early. Bridges were introduced by cyclotrimerization, a reaction that is widely used to make strained rings, as in biphenylenes from the group of Vollhardt,<sup>[9]</sup> indenocorrannulenes from the group of Siegel,<sup>[10]</sup> and helicenes from the group of Starý.<sup>[11]</sup>

Cyclotrimerization offers several advantages over other bridging reactions. The newly bonded atoms are in the correct sp<sup>2</sup> hybridization. Two benzenoid rings are formed with each new bridge, and this provides ample energy to bend the molecule into its cup shape. Both bridging steps are calculated (see the Supporting Information) to be more exothermic (first, −125 kcal mol<sup>−1</sup>; second, −132 kcal mol<sup>−1</sup>) than the cyclotrimerization of 1,2-diethynylbenzene and acetylene into

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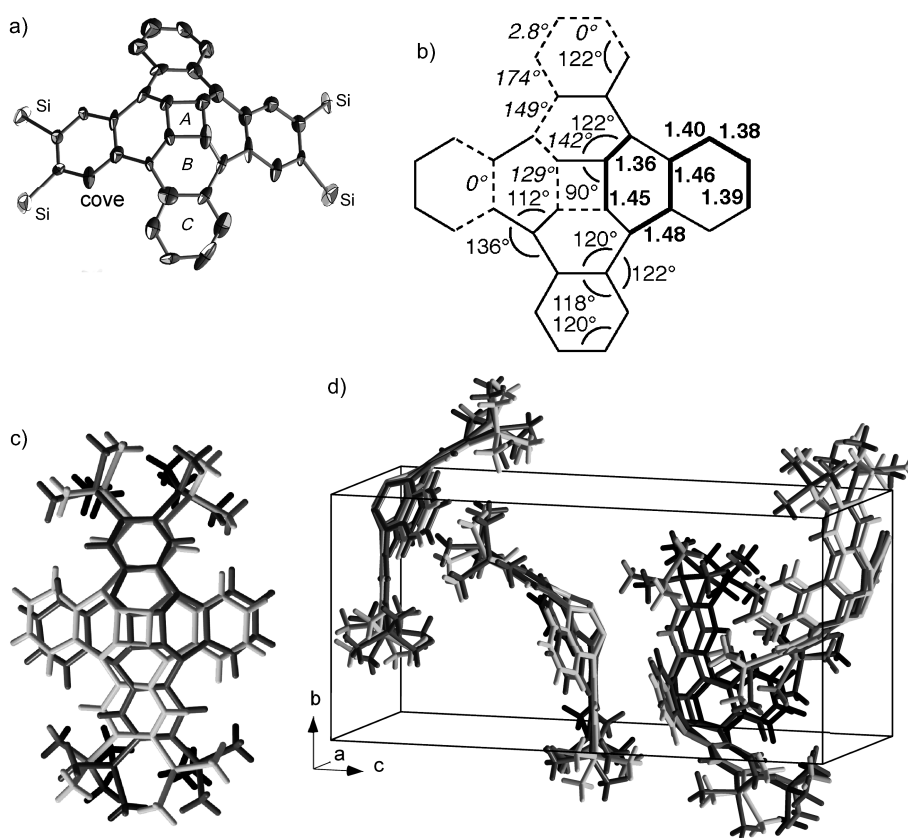
biphenylene ( $-107 \text{ kcal mol}^{-1}$ ), a reaction that works well. The comparison of exothermicities suggested that our cyclotrimerization approach was worth pursuing.

Cyclotrimerization is not, however, ideal. Two arene rings are necessarily *ortho* fused to the quadrannulene core, precluding preparation of the parent quadrannulene. But we reasoned that these appended rings might also offer an advantage; they could protect the otherwise strained olefin bridges from unwanted reactions. We decided to extend this protection to all four of the rim olefins and therefore directed our efforts towards TBQ.

This approach also simplified the preparation of the tetraalkyne precursor **3**, which was synthesized from the naphthoquinone photodimer<sup>[12]</sup> **1** in three steps (Scheme 1). Alkynylation, which required Ce salts to suppress unwanted enolization,<sup>[13]</sup> afforded tetraol **2**. Elimination and desilylation gave **3**. We choose bis(trimethylsilyl)acetylene as the third cyclotrimerization component because the resulting TMS substituents would improve solubility, provide a convenient handle for subsequent chemistry, and facilitate NMR analysis by lowering symmetry. Jonas's catalyst,<sup>[14]</sup>  $\text{CpCo}(\text{CH}_2=\text{CH}_2)_2$ , with bis(trimethylsilyl)acetylene afforded the product as a yet-uncharacterized CoCp complex of  $\text{TMS}_4\text{-TBQ}$ . Oxidation using  $\text{Cp}_2\text{Fe}^+$  liberated, on milligram scale,  $\text{TMS}_4\text{-TBQ}$ .

The structure of  $\text{TMS}_4\text{-TBQ}$  follows from single-crystal X-ray diffraction analysis, mass spectrometry,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and UV/Vis spectrophotometry.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts match those predicted by DFT calculations<sup>[15]</sup> (see the Supporting Information).  $^{13}\text{C}$ , HMQC, HMBC, and COSY spectra (see the Supporting Information) permit full assignment of all  $^1\text{H}$  and  $^{13}\text{C}$  resonances and establish symmetry and connectivity. The central C atoms are more shielded ( $\delta = 145.5 \text{ ppm}$ ) than other pyramidalized but nonconjugated olefin C atoms (ca.  $\delta = 160\text{--}210 \text{ ppm}$ ).<sup>[16]</sup> A strong through-space interaction (NOE) of the abutting H atoms (located in the cove region) establishes their proximity (Figure 1 a).

Single-crystal X-ray diffraction analysis<sup>[17]</sup> shows that  $\text{TMS}_4\text{-TBQ}$  crystallizes without solvent in the chiral  $P2_12_1$  space group (Figure 1). The asymmetric unit contains a single molecule disordered over two orientations (occupancy 0.6:0.4) are rotated (ca.  $8^\circ$ ) about an axis parallel to the pseudo fourfold axis of their central ring (Figure 1 c). The disorder originates from the crystal packing, with no evident



**Figure 1.** a) Thermal ellipsoid plot of the dominant contributor of  $\text{TMS}_4\text{-TBQ}$  crystal (methyl groups and H atoms omitted for clarity) b) Calculated geometry of TBQ (bold type and lines, bond lengths/Å; regular type and arcs, angles; italic type and dashed lines, dihedral angles of contiguous bonds) c) Disorder in the  $\text{TMS}_4\text{-TBQ}$  crystal. The darker shade denotes the residue with higher occupancy. d) The crystal packing, shaded as in C.

$\pi$  stacking or other prominent intermolecular contacts. Two TMS groups from one side of the molecule fill the bowl of another molecule (Figure 1 d). The two TMS groups from the other side are less constrained, and this freedom may contribute to the disorder. Because refinement of the crystal structure required several constraints to model disorder, some geometrical parameters could not be independently refined. For this reason, we discuss measurements from the geometry calculated at the B3LYP/6-311G\*\* level of theory, which is known to provide reliable geometries for many aromatic compounds.<sup>[18]</sup> Nonetheless, the diffraction data agree with the calculated (DFT) geometry and hence prove the structure of  $\text{TMS}_4\text{-TBQ}$ .

The TMS groups only slightly affect the TBQ framework. The substituted and unsubstituted distal rings, C, are similar except that the bonds bearing pairs of bulky TMS groups are stretched ( $1.43 \text{ Å}$ ) relative to their unsubstituted counterparts ( $1.39 \text{ Å}$ ). The C–C bond lengths in  $\text{TMS}_4\text{-TBQ}$  range from  $1.36$  to a high of  $1.48 \text{ Å}$  and are consistent with calculated bond orders, as discussed below.

The bond angles range from a low of  $90^\circ$  in the four-membered ring to a high of  $131^\circ$ . These angles can be transformed into different measures of pyramidalization. We have chosen here that popularized by Haddon, which is based on the  $\pi$ -orbital axis vector, that is, the vector that “makes

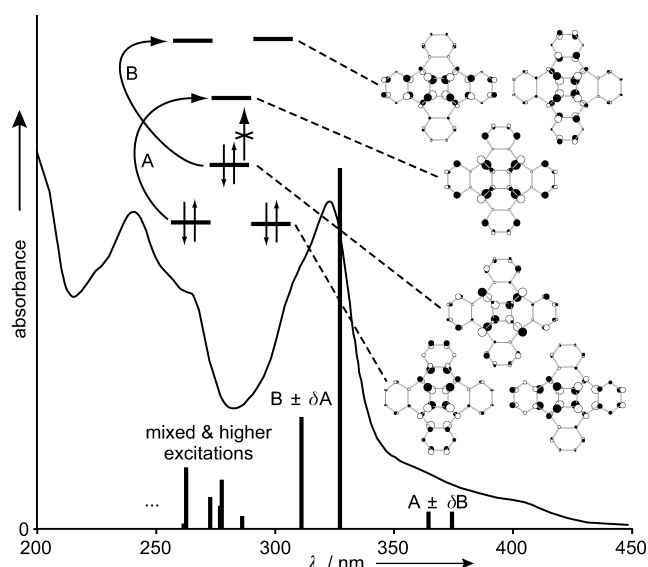
equal angles ( $\theta_{\sigma\pi}$ ) to the three  $\sigma$  bonds at a conjugated carbon atom".<sup>[19]</sup> The angle  $\theta_{\sigma\pi}$ , which varies from  $90^\circ$  for a planar to  $109.47^\circ$  for a tetrahedral C atom, directly reflects pyramidalization.<sup>[19b]</sup> By this token, the central four C atoms are highly pyramidalized:  $\theta_{\sigma\pi} = 107^\circ$ .  $\theta_{\sigma\pi}$  is also related to the degree of hybridization, which is deduced to be  $sp^{2.69}$  for the four central C atoms of TBQ. This distortion makes  $TMS_4$ -TBQ one of the most highly pyramidalized olefins that has been structurally characterized (for example, 9,9',10,10'-tetrahydrodianthracene,  $\theta_{\sigma\pi} = 103^\circ$ , average hybridization  $sp^{2.36}$ ).<sup>[20]</sup>

The bowl depth, defined as the distance between the plane of ring *A* (for notation, see Figure 1a) and the plane of the eight C atoms shared by rings *B* and *C*, of  $TMS_4$ -TBQ is 1.36 Å (as a reference: corannulene, 0.87 Å).<sup>[21]</sup> In corannulenes, this depth is related to the bowl inversion barrier.<sup>[21]</sup> Hopf has calculated the bowl inversion barrier of quadranulene to be 120 kcal mol<sup>-1</sup><sup>[8]</sup> (as a reference: corannulene, 11 kcal mol<sup>-1</sup>).<sup>[21]</sup>

Like corannulene,<sup>[22]</sup> TBQ is a radialene,<sup>[23]</sup> a molecule in which double bonds emanate from all vertices of a ring. Natural bond orbital (NBO) bond orders,<sup>[24]</sup> which we use to support this claim, provide a realistic measure of the order of a bond—single, double, fractional, etc.—from a calculated wave function. The central ring *A* comprises four single bonds (1.45 Å, NBO bond order 1.08). The conjugated medial ring *B* has localized bonds: the four bonds that emanate from the central ring are double (1.36 Å, NBO bond order 1.77) whereas the eight bonds that connect these radial double bonds to the distal rings *C* are single (1.48 Å, NBO bond order 1.08). The distal rings *C* have partially delocalized  $\pi$  bonds (NBO bond orders of 1.26, 1.72, 1.24, and 1.58 and bond lengths of 1.39, 1.38, 1.40, 1.46 Å). The bond shared by rings *B* and *C* is long (1.46 Å), but has normal arene bond character (NBO bond order 1.58), that strain, not electronic structure, causes its elongation.

Nucleus independent chemical shifts (NICS), which probe the diatropic response of the ring current to magnetic fields and are associated with aromaticity,<sup>[25]</sup> support our assessment of the bonding in TBQ. To reduce interference from  $\sigma$  electrons and from other rings, test points were placed on the convex face, 1 Å from the centroid, normal to the ring plane (NICS(1)). The central ring *A* (+4.5 ppm) is closer to [4]radialene (−2.6 ppm) than cyclobutadiene (+16.5 ppm). It is similar to corannulene (+2.6 ppm) and the five-membered ring of  $C_{60}$  (+6.5 ppm). The magnetic properties of the other rings also support the radialene description: medial rings *B* are nonaromatic (−2.3 ppm), and distal rings *C* are fully aromatic (−10.7 ppm; as a reference benzene, −11.1 ppm). The conclusion is clear: TBQ is a benzannulated radialene, not a cyclobutadiene.

The UV/Visible spectrum of  $TMS_4$ -TBQ exhibits maxima at 325 and 244 nm and shoulders at 400 and 260 nm (Figure 2), in addition to weak absorptions between 430 and 350 nm. Time-dependent density functional theory (TD/DFT) calculations on  $TMS_4$ -TBQ reproduce the features above 300 nm quite well, predicting weak absorptions at 376 and 362 nm and strong ones at 326 and 313 nm. These two pairs of transitions derive from excitations A and B in  $C_{4v}$  symmetric TBQ, as depicted in the MO scheme. The HOMO–LUMO transition



**Figure 2.** UV/Visible absorption spectrum and calculated oscillator strengths of  $TMS_4$ -TBQ, molecular orbitals of TBQ, and the electronic excitations that are primarily responsible for the four lowest-energy transitions.

is dipole forbidden and therefore does not appear in the optical spectrum, but it is predicted to be nearly degenerate with the allowed one at 374 nm. Below 300 nm, TD/DFT predicts a dense manifold of excited states that are not dominated by leading excited configurations.

We note also from the MO Scheme in Figure 2 that, as a consequence of the benzannulation, the  $\pi$ -orbital sequence in the central four-membered ring has changed from that of cyclobutadiene, whose high reactivity and biradicaloid character derives from the presence of two close-lying MOs, one of which is doubly occupied while the other is empty (which is also the reason for the rectangular distortion of cyclobutadiene). In TBQ these two MOs are degenerate and both either doubly occupied (HOMO −1) or empty (LUMO +1), and what used to be the highest  $\pi$  MO of cyclobutadiene is now the HOMO of TBQ. These features, which are also typical of [4]radialene, persist in the TMS derivative, which has a nearly square central ring and shows no antiaromatic character.

The vertical gap between the singlet ground state and the lowest triplet excited state is predicted to be 2.68 eV in TBQ and 2.64 eV in  $TMS_4$ -TBQ, much larger than expected for molecules having cyclobutadiene character. The calculated vertical ionization potential of TBQ is low, 7.11 eV, and is lowered by the presence of TMS groups to 6.92 eV (as a reference: pentacene, 6.61 eV<sup>[26]</sup>). Conversely, the electron affinity of TBQ is not unusually high, −0.86 eV in TBQ and −1.00 eV in  $TMS_4$ -TBQ (as a reference naphthalene, ca. 0.6 eV<sup>[26]</sup>).

$TMS_4$ -TBQ is thermally stable to at least 170 °C as a solid (verified by mass spectrometry) and at least 160 °C as a decane solution (verified by UV/Vis). It is stable to visible light and survives brief treatment with TsOH or *t*BuOK in  $CH_2Cl_2$  solution, with some decomposition evident after 10 minutes. It reacts only slowly with air, with slight decom-

position beginning to appear after one week in aerobic  $\text{CH}_2\text{Cl}_2$  at 25 °C

Important questions remain. The role of the distal rings in promoting stability must be elucidated. The reactivity, electronic states, and supramolecular chemistry of the quadrannulene core are essentially unexplored. The nature of the bonding, especially of the C atoms in the central ring, needs further study. Our synthesis, while short, suffers from low yields, especially in the last step. It is, however, flexible and permits the incorporation of substituents, either through substituted naphthoquinones or acetylenes, and may provide access to a new family of quadrannulenes. Even the non-classical,  $O_h$ -symmetric fullerene  $\text{C}_{24}$ , a truncated octahedron,<sup>[27]</sup> now seems less fantastic.

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