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X-ray and Density Functional Theory Structural Study of 1,3,5,7,9-Penta-*tert*-butylcorannulene, $C_{40}H_{50}$

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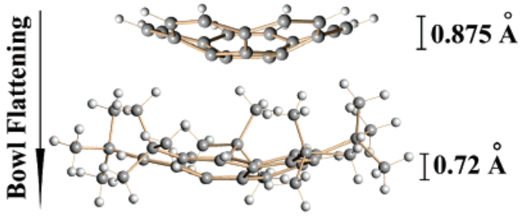
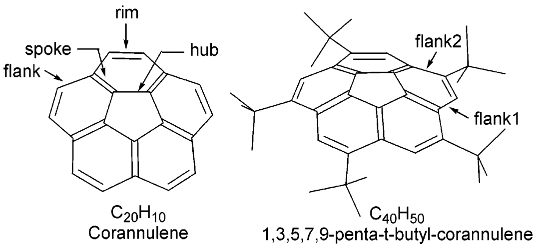


The first X-ray structural characterization of an alkyl-substituted corannulene, namely, 1,3,5,7,9-penta-*tert*-butylcorannulene ($C_{40}H_{50}$), has been accomplished. The addition of bulky *tert*-butyl groups to the corannulene core flattens the bowl and affects the solid-state packing. The presence of two enantiomers, in addition to positional disorder of the $C_{40}H_{50}$ bowls in the solid-state structure, has prevented the acquisition of accurate geometric parameters of this open geodesic polyarene. Therefore, DFT calculations have been used to describe its molecular geometry and to access bond lengths, bond angles, and a bowl depth.

Buckybowls with nonplanar polyaromatic carbon surfaces have attracted special attention in recent years as substructures of fullerenes.[1] Their curvature results in two distinct surfaces, one convex and one concave, that exhibit different properties and reactivity. Corannulene, the smallest C_{60}-fullerene fragment built around a five-membered ring ($C_{20}H_{10}$, Scheme 1), has been a primary focus of theoretical and experimental studies. It was first prepared in 1966 by a multistep conventional organic synthesis.[2] More practical routes to corannulene were developed later using flash vacuum pyrolysis[3] and solution-phase synthetic techniques.[4] The first X-ray crystal structure of $C_{20}H_{10}$ was reported in 1976;[5] however, more recent X-ray measurements at low temperature have improved the quality of structural analysis.[6] To further alter the properties and the reactivity of the bowl, controlled substitution at the rim of corannulene by various substituents has been broadly studied.[7] For example, a systematic spectroscopic and electrochemical investigation of methylated corannulenes revealed trends that are all consistent with an increase in electron density in the core as the number of methyl substituents on the rim increases.[8] In addition, alkyl substitution at the rim of corannulene by methyl groups gradually flattens the bowl and lowers the inversion barrier.

SCHEME 1



As part of our continuing study on the structures and reactivity of open geodesic polyarenes, we have recently turned to 1,3,5,7,9-penta-*tert*-butylcorannulene,[1a,9] a bowl that has bulky groups on all five of the rim double bonds ($C_{40}H_{50}$, Scheme 1). With our interest in the coordination properties of buckybowls,[10] we speculated that crowdedness at the rim might force the metal to complex with less-hindered radial bonds, a type of coordination preferentially exhibited in exohedral metal complexes of

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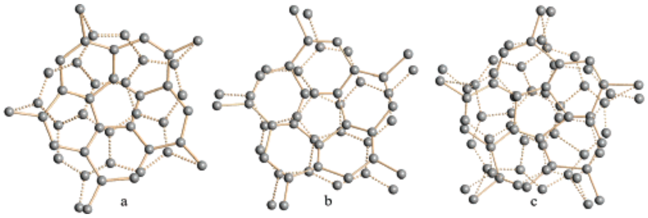

FIGURE 1. (a) Two superimposed enantiomers of $C_{40}H_{50}$. (b) Two orientations of one enantiomer rotated by ca. 18° around the 5-fold molecular axis. (c) Two enantiomers with one of them having two positional orientations. Methyl groups and hydrogen atoms are removed for clarity.

fullerenes.[11] Our preliminary efforts in this direction have confirmed that the *tert*-butyl groups do indeed block coordination to the rim; however, we have not yet succeeded in preparing any metal complexes with $C_{40}H_{50}$ as the ligand. On the other hand, an X-ray crystal structure of this hydrocarbon has been determined, and that makes this the first alkyl-substituted corannulene to be structurally characterized. The 1,3,5,7,9-penta-*tert*-butyl derivative of corannulene was first synthesized by direct Friedel−Crafts alkylation of corannulene more than 10 years ago,[9a] but no structural characterization has been reported.

To access geometric parameters of this bowl and to compare its geometry with that of the parent corannulene, we attempted to crystallize 1,3,5,7,9-penta-*tert*-butylcorannulene using gas-phase sublimation and solution crystal growth techniques. We found that obtaining single crystals of $C_{40}H_{50}$ of sufficient quality is a serious challenge. Numerous attempts to crystallize 1,3,5,7,9-penta-*tert*-butylcorannulene from the gas phase and from several solvent systems were unsuccessful, yielding crystals of poor crystallinity. Finally, colorless plates of the title compound were grown by very slow cooling of a benzene solution containing the title hydrocarbon over the period of several months. Those crystals allowed us to complete the first X-ray diffraction study of an alkyl-substituted corannulene.

X-ray Structural Study. A colorless plate was analyzed at −183 °C and found to be monoclinic: space group $P2_1/c$, $a = 30.190(3)$, $b = 23.5668(18)$, $c = 25.858(2)$ Å, $\beta = 115.333(2)°$, $V = 16629(2)$ Å^3, $Z = 20$. It is worth noting that the same unit cell parameters were obtained for crystals of $C_{40}H_{50}$ deposited from the gas phase at 140 °C; however, the quality of the latter crystals was insufficient to permit structural characterization. The successful crystal structure determination performed on crystals grown from solution revealed an asymmetric unit containing five crystallographically independent molecules of $C_{40}H_{50}$ that are highly disordered. The ideal molecular point symmetry of the 1,3,5,7,9-penta-*tert*-butylcorannulene bowl (C_5) is reduced in the crystal to C_1. For one independent molecule, two enantiomeric forms of the $C_{40}H_{50}$ bowl are centered at the same position with a 65:35% ratio, and this is responsible for the type of disorder shown in Figure 1a. It should be noted here that because the space group is centrosymmetic the total ratio of enantiomers in the crystal is 1:1. As a result, the crystalline compound is a racemic mixture of the two enantiomeric forms.

TABLE 1. Selected Bond Distances (Å) and Angles (deg) in the Structures of $C_{20}H_{10}$ and $C_{40}H_{50}$[a]

	$C_{20}H_{10}$ [6] X-ray	$C_{20}H_{10}$ DFT	$C_{40}H_{50}$ X-ray	$C_{40}H_{50}$ DFT
$C-C_{rim}$	1.3831(15)	1.385	1.40(4)	1.394
$C-C_{spoke}$	1.3790(14)	1.381	1.38(4)	1.375
$C-C_{flank(1)}$	1.4464(16)	1.443	1.46(4)	1.449
$C-C_{flank(2)}$			1.47(4)	1.464
$C-C_{hub}$	1.4151(16)	1.413	1.43(4)	1.409
$C-C-C_{hub-spoke}$	122.92(23)	122.96	123(3)	124.9
$C-C-C_{flank(1)-spoke}$	114.39(22)	114.29	113(3)	112.4
$C-C-C_{flank(2)-spoke}$			113(3)	113.8
$C-C-C_{flank(1)-rim}$	121.95(17)	122.03	124(3)	125.2
$C-C-C_{flank(2)-rim}$			119(3)	119.3
$C-C-C_{flank(1)-flank(2)}$	129.94(35)	130.15	132(3)	133.3
bowl depth	0.875(2)	0.870	0.72(5)	0.677

[a] All distances and angles are averaged. $T = -183$ °C.

In addition, four out of five independent $C_{40}H_{50}$ molecules in the solid-state structure exhibit the positional disorder depicted in Figure 1b. Three of these have a 50:50% occupancy and show molecular rotations of 11, 12, and 18° with respect to the 5-fold axis of the corannulene core. The last independent molecule is the most complex because one $C_{40}H_{50}$ molecule exhibits both types of disorder. It has two enantiomers centered at about the same position, with one of them having two different orientations rotated 9° with respect to each other (Figure 1c). The occupancies are 1/3 for each part in this case.

To derive geometric characteristics of $C_{40}H_{50}$, the corresponding bond distances and angles have to be averaged for all five independent bowls, including their disordered parts (Table 1). A significant variation of all parameters is observed as a result of this extensive disorder and numerous crystal packing influences, and this reduces the ability of the X-ray data to reveal the true, intrinsic carbon−carbon bond distances and angles for the molecule. A comparison of geometric parameters of 1,3,5,7,9-penta-*tert*-butylcorannulene with those of corannulene shows that averaged bond distances and angles are close for the two bowls. The bowl depth[12] of $C_{40}H_{50}$ (0.72 Å), however, is significantly reduced compared to that of $C_{20}H_{10}$ (0.875 Å).

Solid-state packing of the $C_{40}H_{50}$ molecules is very loose, with no close $\pi-\pi$ interactions being detected. The estimated volume per C atom is 20.8 Å^3 vs that of 15.3 Å^3 in the crystal structure of $C_{20}H_{10}$. This difference is attributed to the presence of bulky peripheral groups that prevent close $\pi-\pi$ contacts between the bowls and hamper the efficient solid-state packing. It is known that cyclopentacorannulene ($C_{22}H_{10}$)[13] and other bowls with sufficient curvature, namely, a hemifullerene ($C_{30}H_{12}$)[10b] and circumtrindene ($C_{36}H_{12}$),[14] form aligned stacks through insertion of one bowl into the concave surface of the neighbor. Such stacking is absent in the solid-state structures of corannulene and 1,3,5,7,9-penta-*tert*-butylcorannulene (Figure 2).

Owing to intrinsic problems related to the above-described disorders in the solid-state structure of $C_{40}H_{50}$, we were dissatisfied with the accuracy of the X-ray structural data. Therefore, we turned to DFT calculations to assess the geometry

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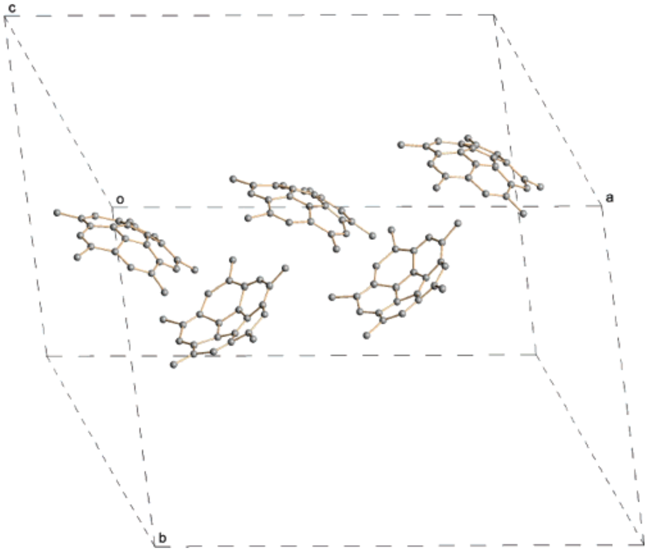

FIGURE 2. Solid-state packing of the $C_{40}H_{50}$ bowls.

of $C_{40}H_{50}$ and to evaluate the effect of rim functionalization of the corannulene core with five bulky alkyl groups.

DFT Study. Calculations were carried out by using a gradient-corrected density functional theory with the hybrid Perdew−Burke−Ernzerhof parameter free exchange−correlation functional (PBE0),[15,16] as implemented in the PC GAMESS[17] suite of programs (Supporting Information). Recently, this approach (PBE0) was shown to be the best choice for theoretical modeling of structures and properties of conjugated aromatic compounds,[18−21] including curved polyaromatic systems.[18,19] Standard 6-31G(d) basis sets that are known to provide an adequate description of curved polyaromatic hydrocarbons [6,22,23] were employed for all atoms. The C_5 point group of symmetry was used for geometry optimizations of the $C_{20}H_{10}$ and $C_{40}H_{50}$ molecules. On the basis of the optimized geometry configurations of both bowls obtained in this work, single-point calculations along with the NBO analysis[24] were performed using the extended 6-311G(d,p) basis sets for all atoms. Bond orders were computed in accordance with the Wiberg technique,[25] as it is incorporated in NBO analysis.

The optimized structural parameters of 1,3,5,7,9-penta-*tert*-butylcorannulene are presented in Table 1 and compared with those of corannulene. Importantly, the use of the PBE0 functional in this work for modeling the geometry of corannulene reproduces the experimental X-ray structure better than all previously reported theoretical methods.[6,26−28] Thus, the greatest difference in bond lengths between our experimental and theoretical data is now only 0.005 Å vs 0.01 Å for the DFT/B3LYP/6-31G(d) level of calculations.[6] This justifies the use of the above functional for accessing the geometry of $C_{40}H_{50}$, for which the X-ray data failed to provide sufficiently precise structural characteristics.

In this context, a direct comparison of calculated parameters for the two bowls is informative because it allows us to estimate the influence of bulky substituents on the corannulene core in $C_{40}H_{50}$. First, because *tert*-butyl groups are attached to one side of the rim bonds of $C_{40}H_{50}$ only, there are two sets of nonequivalent flank bonds (Scheme 1), with the flank(1) bond being noticeably shorter than flank(2) (1.449 vs 1.464 Å). Second, the latter is elongated compared to the flank bond of corannulene (0.021 for flank(2) vs only 0.006 Å for flank(1)). The rest of the bond differences are almost negligible. Although the rim carbon−carbon bonds are elongated (0.009 Å), the hub and spoke bonds are slightly shortened (by 0.004 and 0.006 Å, respectively), when compared to the corresponding bond lengths of the unsubstituted corannulene.

As expected, an addition of five *tert*-butyl groups to the corannulene core causes a noticeable reduction in curvature of the $C_{40}H_{50}$ bowl, as confirmed both experimentally and computationally. Although the bowl depth of $C_{40}H_{50}$ estimated by DFT (0.677 Å) seems smaller than that obtained from X-ray data (0.72(5) Å), the difference is statistically insignificant, if the above large standard deviation is taken into account. For comparison, the bowl depth of corannulene calculated at the same level of theory (0.870 Å) is very close to the experimental value of 0.875(2) Å.

In addition, an influence of bulky substituents on the electronic structure of $C_{40}H_{50}$ has been examined by the NBO charge distribution and bond-order analysis. An introduction of *tert*-butyl groups to the rim leads to redistribution of electron density in $C_{40}H_{50}$ compared to that in $C_{20}H_{10}$. This is clearly seen from a comparison of charges for the flank−rim carbon atoms. The latter are equal to −0.180 in $C_{20}H_{10}$ but are nonequivalent in $C_{40}H_{50}$, with values of −0.224 and +0.004 for the flank(1)−rim and flank(2)−rim carbon atoms, respectively. This shows that the *tert*-butyl group acts as a weak acceptor (in contrast to hydrogen) in $C_{40}H_{50}$, which is also reflected in a slight decrease of negative charges at the flank−spoke and hub−spoke carbon atoms in the penta-substituted *tert*-butylcorannulene (Supporting Information). The same trends were observed for the bond orders in corannulene and 1,3,5,7,9-penta-*tert*-butylcorannulene. The presence of the *tert*-butyl groups results in a slight decrease of bond orders for the rim, hub, and flank (both types) carbon−carbon bonds. Moreover, the flank(2) bond order becomes very close to that of the hub bond. At the same time, the spoke bond order is increased.

The flattening of the bowl is expected to reduce quite significantly the energy barrier for bowl−bowl inversion.[29] Seiders et al. have found that the inversion barriers for a wide

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range of substituted corannulenes vary in direct proportion to the fourth power of the bowl depths.[7b] Accordingly, a reduction in bowl depth from 0.875 Å for $C_{20}H_{10}$ to 0.72 Å for $C_{40}H_{50}$ (X-ray values for both, Table 1) should reduce the energy barrier for bowl−bowl inversion to 46% of the value for the unsubstituted parent hydrocarbon. Applying the quartic relationship of Seiders et al. to the calculated bowl depths for corannulene and 1,3,5,7,9-penta-*tert*-butylcorannulene (0.870 and 0.677 Å, respectively, Table 1) predicts a reduction to 37% of the value for the inversion barrier of unsubstituted corannulene. DFT calculations on the geometry-optimized transition states for both bowl−bowl inversions predict a reduction of 44% from the barrier for $C_{20}H_{10}$ (10.3 kcal/mol) to that for $C_{40}H_{50}$ (4.5 kcal/mol). The experimental determination of energy barriers for bowl−bowl inversions by variable-temperature NMR measurements requires the presence of one or more substituents that contain diastereotopic atoms or groups of atoms.[7b,29] Unfortunately, 1,3,5,7,9-penta-*tert*-butylcorannulene has no such diastereotopic probes, so no experimental test of these predictions can be made.

In summary, the first structural characterization of 1,3,5,7,9-penta-*tert*-butylcorannulene by X-ray diffraction and DFT methods reveals the geometric and electronic structure of the bowl. A comparison of penta-substituted *tert*-butylcorannulene with the parent corannulene shows that addition of bulky peripheral groups significantly flattens the bowl and prevents close bowl−bowl $\pi-\pi$ interactions, which affects the solid-state packing of the $C_{40}H_{50}$ molecules. The steric crowdedness at the rim and induced electronic changes at the corannulene core make the title polyarene a very interesting ligand to study for metal binding reactions.

Experimental Section

Synthesis of $C_{40}H_{50}$. Aluminum chloride (8.0 mg, 0.06 mmol) was added, with stirring, to a solution of corannulene (100 mg, 0.4 mmol) in 8.0 mL of *tert*-butyl chloride at 0 °C under nitrogen. A pink-colored suspension developed immediately. Catalytic amounts of aluminum chloride were periodically added to the flask as the pink color discharged with time. After 2 h, the reaction mixture was allowed to warm to room temperature, and stirring was maintained at that temperature for two more days. The reaction mixture was then diluted with methylene chloride and washed with 3 × 20 mL of 10% hydrochloric acid and 3 × 20 mL of saturated sodium chloride solution. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with 3:1 hexane/methylene chloride as eluant, followed by recrystallization from ethanol and hexane (1:1) to give 145 mg of 1,3,5,7,9-penta-*tert*-butylcorannulene as a colorless solid (yield 68%): mp 380 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 5H), 1.72 (s, 45H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 135.2, 128.1, 123.2, 37.8, 33.2; MS (EI, 70 eV) *m*/*z* (relative intensity) 530 (62, M^+), 515 (37), 305 (11), 291 (44), 250 (53), 207 (18), 57 (100); HRMS (EI, 70 eV) calcd for $C_{40}H_{50}$ (M^+) 530.3912, found 530.3912.

X-ray Data for $C_{40}H_{50}$: $M_r = 530.80$, colorless plate, 0.30 × 0.17 × 0.04 mm, monoclinic, space group $P2_1/c$, $a = 30.190(3)$, $b = 23.5668(18)$, $c = 25.858(2)$ Å, $\beta = 115.333(2)°$, $V = 16629(2)$ Å^3, $Z = 20$, $T = 90(2)$ K, $\rho_c = 1.060$ g cm^{-3}, $\mu = 0.059$ mm^{-1}, $\theta_{max} = 22.51°$. Bruker SMART APEX CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct methods and refined with the Bruker SHELXTL (version 6.1) software package. Data were corrected for absorption effects using the empirical methods SADABS (min/max apparent transmissions are 0.9825/0.9976). All C atoms were refined isotropically. All hydrogen atoms were included at idealized positions for structure factor calculations. Full-matrix refinement on F^2 converged at $R1 = 0.1692$ and $wR2 = 0.2990$ for 13 093 reflections and 1804 parameters with $I > 2\sigma(I)$. $R1 = 0.2313$, $wR2 = 0.3267$ for 21 692 unique reflections. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.403 and −0.430 e/Å^3. GOF = 1.122.

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Supporting Information Available: An X-ray crystallographic file, in CIF format; computation details; and tabular materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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