The first crystal structure characterization of a semibuckminsterfullerene, and a novel synthetic route

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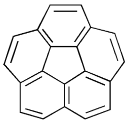
Tetrabromosemibuckminsterfullerene 6, obtained by a novel synthetic route, is converted to the tetramethyl derivative 7; X-ray crystal structure determination of the latter reveals a highly nonplanar, bowl-shaped molecule with solvating CCl_4 molecules separating the hydrocarbon moieties.

The considerable attention given to C_{60} and the family of fullerenes has led to renewed interest in curved-surface polynuclear aromatic hydrocarbons known as fullerene fragments or 'buckybowls.'[1] Corannulene (**1**), first synthesized in the 'pre-fullerene' era, is the smallest member of this family.[2] Several other buckybowls are now known,[1] including two semibuckminsterfullerenes $C_{30}H_{12}$ (**2**[3] and **3**[4]) and the largest to date, circumtriindene $C_{36}H_{12}$ (**4**).[5] Most of the buckybowls were obtained by flash vacuum pyrolysis (FVP) which involves high temperatures and separation of the precursor molecules in the gas phase; *i.e.* factors believed to be important for the formation of these strained systems.[1] Only recently have more practical, condensed phase alternative synthetic protocols developed.[3b,c,6–8] In this communication we report a novel, convenient route to tetrasubstituted semibuckminsterfullerene **2**, as well as an X-ray crystal structure determination of the tetramethyl derivative. The latter represents the first X-ray crystallographic results for a semibuckminsterfullerene.



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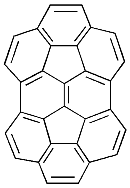

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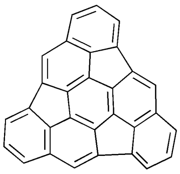

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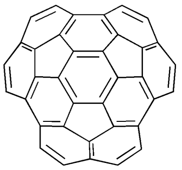

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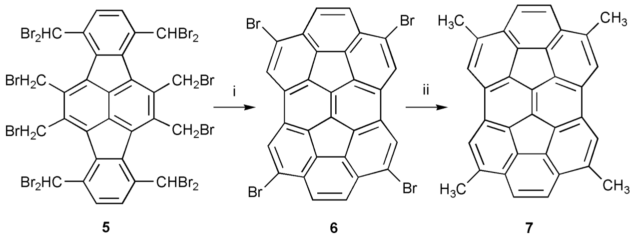
Recently we discovered that carbenoid coupling of the dibromomethyl groups of tetrakis(dibromomethyl)fluoranthene leads to the formation of 1,2,5,6-tetrabromocorannulene in high yields.[8] Application of this protocol to dodecabromide **5** is also successful in producing the corresponding tetrabromosemibuckminsterfullerene **6**, although in more modest yield (Scheme 1). Thus, 30 min reflux of **5** in a 3:1 mixture of dioxane and water with sodium hydroxide provides *ca.* 25% yield of **6**.[9] Although the yield of this transformation is similar to that of McMurry coupling,[3b,c] it nonetheless represents a major improvement due to convenience, low cost, and greater reproducibility. The previous method requires long periods of slow addition of the substrate to the reaction mixture (high dilution conditions), as well as strict anhydrous conditions and a deoxygenated environment.[3b,c] None of those requirements are necessary for the present method, since it only involves a short period of reflux in aqueous solvent. Hence this method has much greater potential for the large scale production of **2** and its derivatives.



5 6 7

Scheme 1 *Reagents and conditions*: i, NaOH, dioxane–water (3:1), reflux 30 min, 26%; ii, $AlMe_3$, $NiCl_3(dppp)$, DME, reflux 12 h, 80%.

Since the carbenoid coupling of **5** leads cleanly to symmetrically substituted **6**, it provides an opportunity for further elaboration of this novel molecule. For example, the four bromine atoms in **6** can easily be replaced by methyl groups leading to **7**.[10] We have been attempting X-ray diffraction studies of semibuckminsterfullerene **2** for some time. Several crystals of **2** were grown from various solvent systems, but they failed to produce useful X-ray diffraction data as a result of poor scattering or multiple twinning. Thus we sought to finally solve this problem with **7** since it produced attractive crystals from a variety of solvents. But again we encountered difficulties—what appeared to be crystals of high quality under the microscope did not produce good diffraction data. Finally we succeeded with a crystal grown by slow evaporation of a carbon tetrachloride solution.[11]

Crystal structure determination shows that **7** crystallizes with two symmetrically independent solvating carbon tetrachloride molecules (Fig. 1). The ideal molecular point symmetry of **7**(C_{2v}) is reduced in the crystal to C_s. The crystallographic mirror plane passes through the carbon atoms and four chlorine atoms of the solvating CCl_4 molecules and bisects the three central carbon–carbon bonds of **7**. The hydrocarbon part exhibits very significant curvature, forming a well developed bowl as predicted for **2** earlier by theory.[3a] The pyramidalization angles defined by the π-orbital axis vector method (POAV)[12] are highest at the central carbon atoms, then

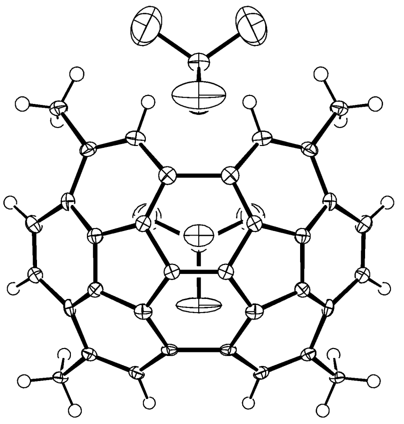


Fig. 1 ORTEP plot of **7***$2CCl_4$ with 30% thermal elipsoids.

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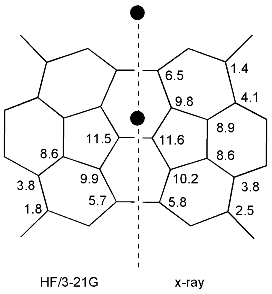

Fig. 2 POAV pyramidalization angles calculated for the crystal structure (right) and for the *ab initio* HF/3-21G optimized geometry (left) of **7**. The dotted line describes the crystallographic mirror plane and the dots represent the solvating CCl_4 molecules.

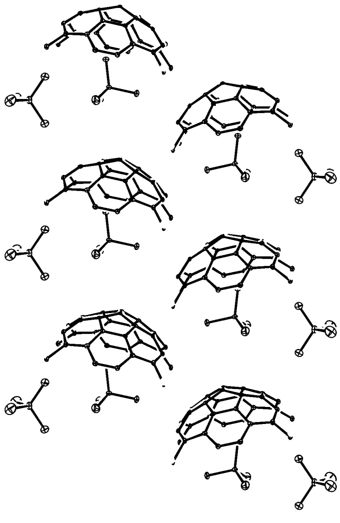

Fig. 3 Crystal packing pattern in **7***$2CCl_4$. Hydrogen atoms omitted for clarity.

gradually decrease when going toward the rim (Fig. 2). In the region of maximum curvature the pyramidalization of the carbon atoms is quite comparable with that of buckminsterfullerene which has a pyramidalization angle of 11.6°.[12] Comparison of the POAV angles calculated for **7** in the crystal with those based on the *ab initio* optimized geometry of the isolated molecule[13] not only demonstrates the adequacy of the theoretical model, but also suggests that crystal packing forces have very little effect on the curvature of this strained molecule.

Buckybowls have the potential to stack in a concave to convex fashion. Of the very few X-ray crystal structure determinations reported to date, stacking was found in cyclopentacorannulene $C_{22}H_{10}$[14] as well as in $C_{36}H_{10}$,[15] while it is absent in the crystals of corannulene.[16] The present case represents a novel situation, since **7** co-crystallizes with carbon tetrachloride molecules (Fig. 3). One of the solvating CCl_4 molecules separates two molecules of **7** with one of the chlorine atoms in the concave orientation and three chlorine atoms on the convex side. The 'concave' chlorine atom forms twelve nonbonding C···Cl distances in the range of 3.262(7) to 3.501(7) Å, roughly equal or shorter than the sum of the respective van der Waals radii, and in addition, it has six slightly longer C···Cl distances in the range 3.582(7) to 3.747(7) Å. As a consequence of the 'stuffing' of **7** with the solvent molecule, close contacts between the hydrocarbon moieties are minimized. The closest of these, 3.528(9) Å, is between the methyl group carbons, and the nearest intermolecular distance between bowl carbon atoms is 3.654(10) Å. Thus, this solid state arrangement is not, strictly speaking, 'bowl-to-bowl stacking' even though some piling of the solvated molecules is evident.[17]

In conclusion, tetrabromo- and tetramethylsemibuckmisterfullerenes **6** and **7** can be prepared by a convenient, non-pyrolytic route that allows for scale-up. Moreover, the crystal structure of **7** shows that the curvature of this system, at least in the interior region of maximum curvature, is comparable to buckminsterfullerene.

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9 **6**: Orange crystals (from toluene). Darkens gradually above 300 °C, but does not melt up to 350 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 4H), 7.69 (s, 4H). ^{13}C NMR (75.44 MHz, $CDCl_3$) δ 128.94, 127.97. Quaternary carbons not detected due to the very limited solubility of **6** in common deuterated solvents. HRMS: calcd for $C_{30}H_8Br_4$ 683.7359; found 683.7350.

10 **7**: Yellow solid (sublimation). Gradually darkens above 350 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (4H, broad d, J = 0.9 Hz), 7.55 (4H, s), 2.64 (12H, d, J = 0.9 Hz). ^{13}C NMR (75.44 MHz, $CDCl_3$) δ 141.12, 137.05, 136.71, 136.36, 128.14, 124.67, 124.61, 124.57. HRMS: calcd for $C_{34}H_{20}$ 428.1575; found 428.1573.

11 *Crystal data*: $C_{36}H_{20}Cl_8$, FW = 736.12; orthorhombic, $Cmc2_1$; a = 16.2594(8), b = 20.0097(10), c = 9.2417(5) Å; V = 3006.7(3) Å^3; Z = 4; D_{calc} = 1.626 g cm^{-3}; $F(000)$ = 1488; T = 173 K; R = 0.0761, Rw = 0.218 for 1841 observed data. Intensity data were collected on a Bruker CCD-1000 diffractometer equipped with Mo-Kα radiation (λ = 0.71073 Å). Hydrogen atoms were placed in calculated positions. CCDC 182/1834. See http://www.rsc.org/suppdata/cc/b0/b007771m/ for crystallographic data in .cif format.

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