Corannulenes

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A Buckybowl with a Lot of Potential: C_5-$C_{20}H_5(CF_3)_5$**

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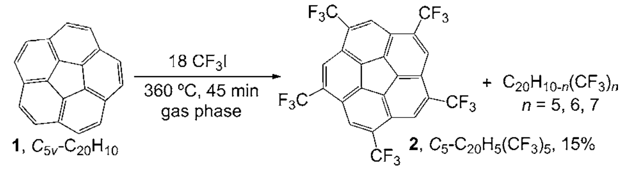
Corannulene (**1**) is a bowl-shaped polycyclic aromatic molecule composed of five fused benzenoid rings that has C_{5v} symmetry and is a hydrogen-terminated fragment of closed-cage carbon clusters, such as C_{60}. It was first prepared in 1966 by a 17-step synthesis with an overall 0.4 % yield.[1] More practical syntheses have been developed in the past decade,[2] and the greater availability of **1** has led to extensive studies of the structure,[3] molecular dynamics,[4] reduction,[5] coordination,[6] and other physicochemical properties of corannulene derivatives,[2,7–9] including potentially useful compounds and materials, such as molecular tweezers,[10,11] electroluminophores for OLEDs,[12,13] and organic semiconductors.[14]

We report herein the synthesis (Scheme 1 and Supporting Information) and characterization of the first perfluoroalkylcorannulene, C_5-$C_{20}H_5(CF_3)_5$ (**2**). The pale-yellow crude product consisted of a mixture of air-stable $C_{20}H_{10-n}(CF_3)_n$ derivatives that are soluble in toluene and CH_2Cl_2 (^{1}H NMR analysis showed complete conversion of **1**). The negative-ion APCI mass spectrum in Figure 1 (see also the Supporting Information, Figure S1) exhibits two main peaks assigned to $C_{20}H_5(CF_3)_5^-$ and $C_{20}H_4(CF_3)_6^-$ and a much smaller peak assigned to $C_{20}H_3(CF_3)_7^-$. HPLC separation of the product mixture with a Cosmosil Buckyprep column (used here for the first time for corannulene derivatives) resulted in several fractions, including the abundant product **2** with $t_R = 4.5$ min (Figure 1). The yield of isolated **2** was 15 %.[15]



Scheme 1. Gas-phase trifluoromethylation of corannulene.

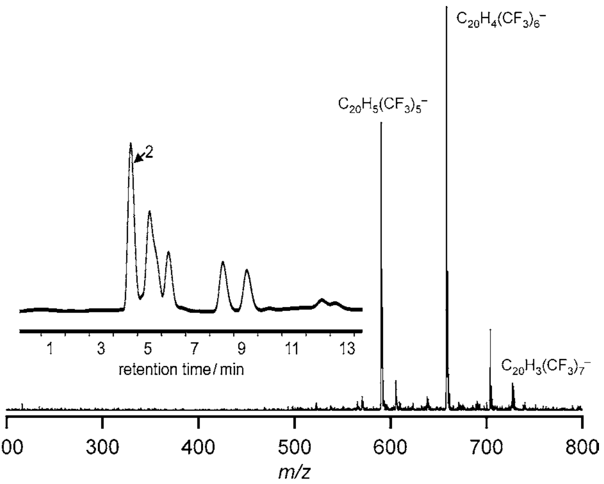


Figure 1. NI-APCI mass spectrum and Cosmosil Buckyprep HPLC trace (inset) of the crude product $C_{20}H_{10-n}(CF_3)_n$ ($n = 5, 6, 7$).

Compound **2** was the first to be characterized because of its high abundance, its high symmetry, and because it formed single crystals suitable for an X-ray diffraction study. Other components of the product mixture will be reported later once they are more extensively purified and characterized. Figure 2 shows the ^{1}H and ^{19}F NMR spectra, APCI mass spectrum, and HPLC trace of HPLC-purified **2**. The mass spectrum exhibits an $m/z = 590$ peak assigned to molecular anion $C_{20}H_5(CF_3)_5^-$ (its isotope distribution matches the expected pattern). The ^{1}H NMR spectrum consists of a $\delta = 8.53$ unresolved apparent septet ($^4J_{HF} = {}^5J_{HF} = 1.2$ Hz); the ^{19}F spectrum consists of a $\delta = -61.25$ triplet ($J_{HF} = 1.2$ Hz). The internal intensity standard 1,4-$C_6H_4(CF_3)_2$ was used to demonstrate that molar ratio F/H = 2.9 (calcd 3.0). The NMR results confirmed the proposed molecular formula and demonstrated that **2** must have C_5 symmetry.

Slow evaporation of a benzene solution of **2** produced thin needles suitable for X-ray diffraction.[15] Despite the tetragonal symmetry of the unit cell, the molecule has no crystallo-

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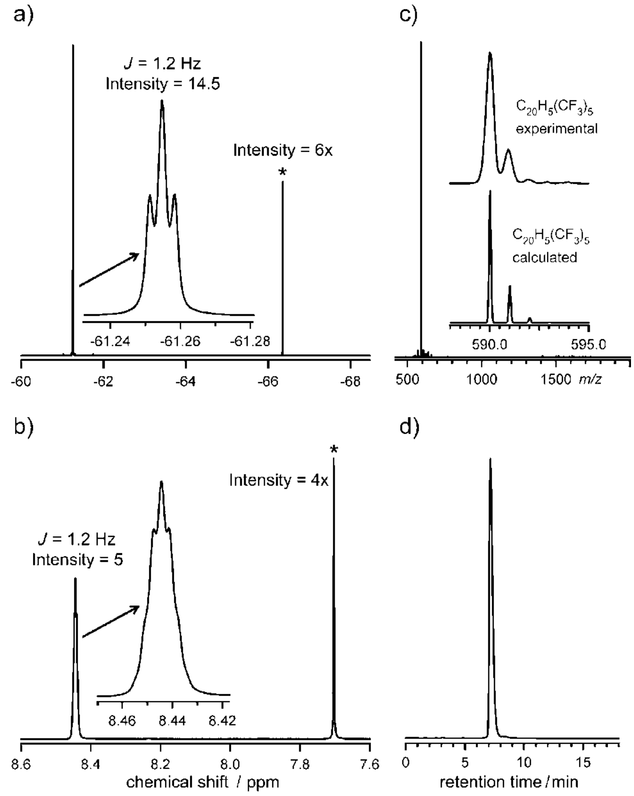

Figure 2. a) ^{19}F and b) ^{1}H NMR spectra of **2** (peaks marked with asterisks correspond to the 1,4-$C_6H_4(CF_3)_2$ internal intensity standard); c) NI-APCI mass spectrum of **2**; d) HPLC trace of **2** (100% heptane; 7 mL min^{-1}).

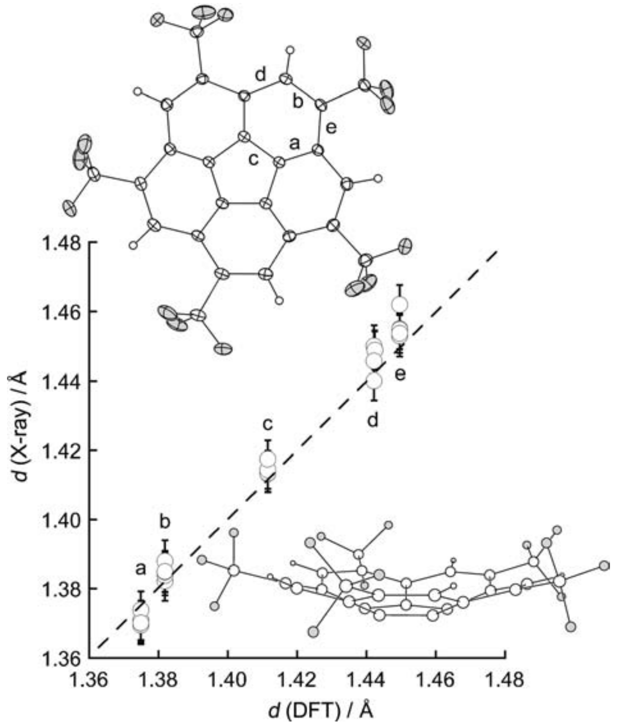

Figure 3. Two views of the structure of **2** (ellipsoids set at 50% probability for non-H atoms in the upper drawing) and a plot of X-ray versus DFT-predicted C–C distances d (error bars are $\pm 3\sigma$).

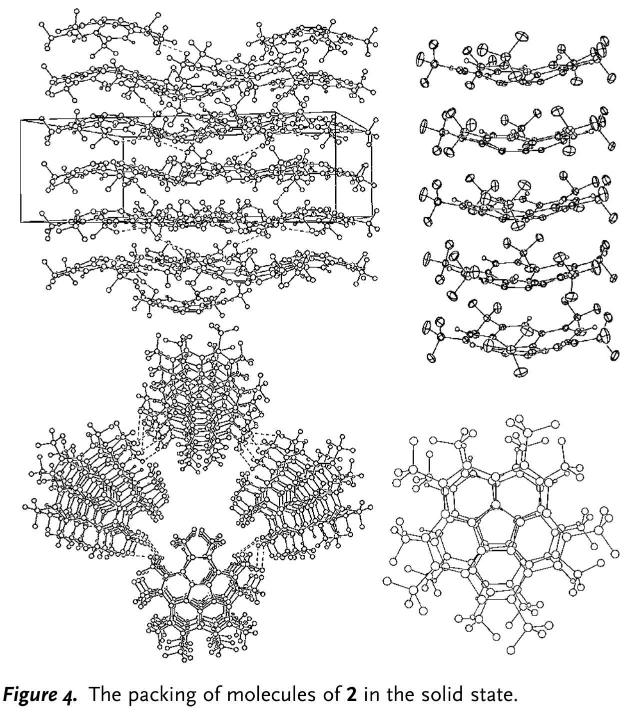

Figure 4. The packing of molecules of **2** in the solid state.

graphically imposed symmetry. Figure 3 shows two views of the bowl-shaped molecular structure (idealized C_5 symmetry) and a graph displaying the ranges of distances of the five types of C–C bonds in **2**. The graph also displays the B3LYP-D/def2-TZVP-predicted C–C distances, which are in excellent agreement with the X-ray determined distances.

The standard errors (σ) for individual C–C distances range from 0.0018 to 0.002 Å. The central pentagon in the X-ray structure is planar within ±0.001 Å. The depth of the bowl is determined by the mean perpendicular distance of the rim carbon atoms from the least-squares plane of the central pentagon. This mean distance is 0.788 Å; the standard deviation for the 10 distances is 0.015 Å. The DFT bowl depths are 0.910(2) Å for **1** and 0.859(7) Å for **2**. The bowl depth in the X-ray structure of **2** is smaller (that is, the bowl is flatter) than in the DFT structure at least in part because of the crystal packing arrangement. As previously shown,[16] bowl depth depends on the type of substituent, and it can range from 0.875(2) Å for **1**[17] to 0.72 Å for C_5-$C_{20}H_5(t\mathrm{Bu})_5$[18] to 0.51 Å for $C_{20}Cl_{10}$.[19]

Drawings of the solid-state packing of molecules in the X-ray structure of **2** are shown in Figure 4. There are columns of **2** stacked like shallow bowls (3.796 Å between the pentagons of molecules in the stack; this also results in essentially parallel hexagon···hexagon distances of 3.5–3.6 Å). Alternate stacks face opposite directions along the crystallographic *c* axis. Within each stack, every molecule is rotated 5.8° with respect to the enantiomeric molecules above it and below it. There is a narrow, empty channel along the *c* axis through the centers of parallel unit cells. The adjacent pentagon-centroid···pentagon-centroid distance is 12.271 Å (note that these pairs of centroids are not in a common plane parallel to the crystallographic *ab* plane). The centroid···centroid distance between opposite pentagons is 17.237 Å (these two centroids are in a common plane parallel to the *ab* plane). The distances between the four closest F atoms are 4.653(2) (adjacent stacks) and 6.232(2) Å (opposite stacks). It is likely that the alternation of positive and negative charge around the rim in **2** is responsible for the unusual, highly regular stacking arrangement. Despite its high symmetry and the lack of substituents larger than H atoms, corannulene itself does not form stacks, and its DFT-predicted dipole moment, 2.19 D, is actually larger than the 1.34 D DFT-predicted dipole moment for **2**. This is discussed in more detail in the Supporting Information.

Cyclic voltammetry of **1** and **2** in CH_3CN (Figure 5) reveals that substitution of five H atoms for electron-withdrawing CF_3 groups resulted in an unprecedented 0.95 V anodic shift of the $E_{1/2}$ value for the first reduction of **2** relative to **1** in CH_3CN (CV and SW voltammetry results are given in the Supporting Information, Table S1). Redox potentials for **1** have been reported previously.[20–22] Such a large anodic shift for **2** exemplifies the ability of perfluoroalkyl (R_F) substituents to significantly alter the electronic properties of organic compounds; similar, albeit weaker, effects were observed when several R_F groups were introduced into various polycyclic aromatic molecules[23] or fullerenes.[24] The reduction of **2** in CH_3CN appears to be irreversible (note the shoulder at ca. 1.0 V vs. $\mathbf{1}^{0/-}$). However, the reduction of **2** is reversible in o-$C_6H_4Cl_2$. It was not possible to compare **2** to **1** in o-$C_6H_4Cl_2$ because the cathodic potential limit of o-$C_6H_4Cl_2$ is not negative enough to observe the reduction of **1**.

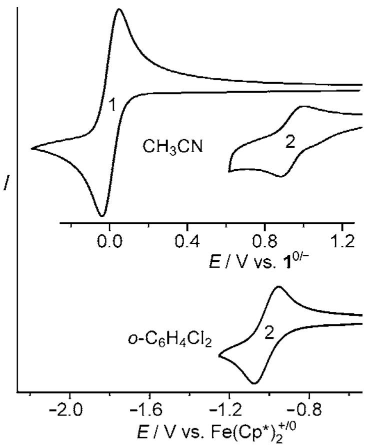

Figure 5. Cyclic voltammograms (scan rate 100 mV s^{-1}) of **1** and **2** in CH_3CN (0.1 M nBu$_4$NClO$_4$) and **2** in o-$C_6H_4Cl_2$ (0.1 M nBu$_4$NBF$_4$). All three CVs are shown relative to each other on the lower potential scale (vs. internal $Fe(Cp^*)_2{}^{+/0}$). The relative potentials of **1** and **2** in CH_3CN are also shown on the upper potential scale with $E_{1/2}(1^{-/0})$ defined as 0.0 V.

To study the effect of different substituents, we calculated $E_{1/2}$ values in CH_3CN and gas-phase electron affinities (EAs) for $C_{20}H_{10-n}X_n$ derivatives with X = CH_3, Cl, F, CF_3, and CN and n = 0–10 by DFT. The results are shown in Figure 6. Two experimental $E_{1/2}$ values are also included (for a list of EA and $E_{1/2}$ values and other details about the DFT calculations, see the Supporting Information).

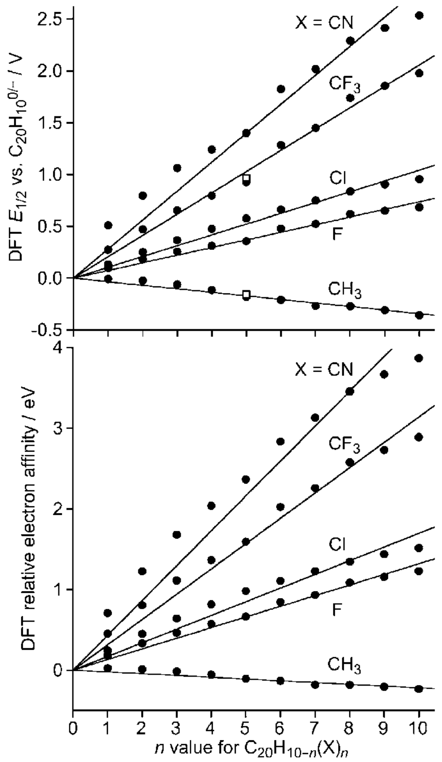

Figure 6. DFT-predicted $E_{1/2}$ values (CH_3CN) and electron affinities of $C_{20}H_{10-n}X_n$ compounds. Two experimental points (□) are shown in the $E_{1/2}$ graph for **2** (this work) and for C_5-$C_{20}H_5(CH_3)_5$ (Ref. [21]).

An estimated value of the EA of **1**, determined using the rates of competitive dissociations of mass-selected cluster ions, is 0.50(1) eV;[25] our DFT-predicted value is 0.52 eV. The experimental difference in the $E_{1/2}$ values for **1** and **2** is 0.95 V; the DFT $\Delta E_{1/2}$ is 0.93 V. The experimental $\Delta E_{1/2}$ for **1** and C_5-$C_{20}H_5(CH_3)_5$ in CH_3CN is −0.15 V;[21] the DFT value is −0.18 V. This agreement suggests that our other predicted values might be reliable to ±30 mV.

There is a roughly linear dependence of $\Delta E_{1/2}$ and ΔEA on the value of n for each of the five substituents. Of the substituents studied, CF_3 groups have the second largest effect on $E_{1/2}$ and EA after CN groups. Note that fluorine atoms have a much smaller effect than CF_3 groups (and even a smaller effect than chlorine atoms), the opposite of what was found for $C_{60}F_n$ vs. $C_{60}(CF_3)_n$.[24] The difference is attributable to: 1) substituents on C(sp^2) atoms in conjugation with an extensive π system (in corannulene) vs. substituents on C(sp^3) atoms (in C_{60}); and 2) the fact that F atoms are capable of π donation and CF_3 groups are not.

The DFT-predicted average $E_{1/2}$ increment of 0.20 V per CF_3 group suggests that at least one isomer of $C_{20}H_3(CF_3)_7$ will be an even stronger electron acceptor than C_{60}, which is commonly used as an electron acceptor for many applications. Preliminary square-wave voltammetry data for a mixture of $C_{20}H_{10-n}(CF_3)_n$ derivatives (Supporting Information, Figure S2) suggest that this prediction may be correct.

The addition patterns for $C_{60}(CF_3)_n$ derivatives play a more important role in determining reduction potentials than the number of CF_3 groups.[24] Will this also be true for corannulene derivatives? The only experimental data that bear on this question involve two isomers each of $C_{20}H_8(CH_3)_2$ ($E_{1/2} = -0.06$ and -0.07 V vs. $\mathbf{1}^{0/-}$) and $C_{20}H_6(CH_3)_4$ ($E_{1/2} = -0.09$ and -0.12 V vs. $\mathbf{1}^{0/-}$).[21] As these cathodic shifts are very small, the comparison is inconclusive. We are in the process of calculating $E_{1/2}$ and EA values for various isomers of $C_{20}H_{10-n}X_n$ and these will be reported in the full paper.

The results presented herein demonstrate that the electronic properties of corannulene can be fine-tuned in a predictable manner over a broad range of positive as well as negative potentials relative to $C_{20}H_{10}{}^{0/-}$. The compound C_5-$C_{20}H_5(CF_3)_5$ is the first member of a family of corannulene-based strong electron acceptors. Further work on other $C_{20}H_{10-n}(CF_3)_n$ compounds is in progress.

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[15] See Supporting Information for experimental details. Crystal data for $C_{20}H_5(CF_3)_5$: $M_r = 590.29$ g mol^{-1}, tetragonal, $P\bar{4}2_1c$, $a = 23.465(3)$, $b = 23.465(3)$, $c = 7.5919(9)$ Å, $V = 4180.1(9)$, $Z = 4$, $T = 110(2)$ K, 8082 reflections, 6906 independent reflections, 382 parameters, R_1 ($I > 2\sigma(I)$) = 0.0457, $wR_2 = 0.1190$, Bruker D8 goniometer with APEXII CCD detector, synchrotron source ($\lambda = 0.39739$ Å; Si(111) monochromator). A semiempirical absorption correction was applied using SADABS. Refined using SHELXTL. CCDC 861064 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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