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Electron Acceptors

$C_{20}H_4(C_4F_8)_3$: A Fluorine-Containing Annulated Corannulene that Is a Better Electron Acceptor Than C_{60}**

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There has been increased interest in the design and applications of small polyaromatic molecules for energy conversion and storage, organic transistors and organic light-emitting diodes (OLEDs), and other emerging areas of modern technology.[1] In particular, functionalized polycyclic aromatic hydrocarbons (PAHs) have demonstrated excellent electrical mobilities in organic thin-film transistors, in some cases even under ambient conditions.[2] It has been suggested that the air stability of such organic materials is correlated with their electronic properties and, more specifically, with a high electron affinity.[3] Until recently, geodesic PAHs, such as corannulene[4] and sumanene,[5] as well as their numerous derivatives, have not been seriously considered for optoelectronic applications because 1) they typically possess very low electron affinities (e.g. $\text{EA}(C_{20}H_{10}) = 0.5(1)$ eV),[6] and 2) laborious multistep syntheses with moderate-to-low yields made them practically unavailable for such studies.[7] Although the low availability of sumanene remains unchanged, significant progress has been made recently in the large-scale synthesis of corannulene.[8] Furthermore, our recent studies demonstrated that functionalization of corannulene with electron-withdrawing groups (EWGs) results in a drastic enhancement of its electron-acceptor properties.[9] In particular, a 950 mV positive shift in the reduction potential for the trifluoromethylated derivative $C_{20}H_5(CF_3)_5$ relative to the parent $C_{20}H_{10}$ was observed. We also predicted that other EWGs, including halogen atoms or a cyanide group, could be used to enhance the electron affinity of corannulene. The nearly linear correlation between the number of EWGs and the electron affinity (reduction potential) of the corresponding EWG-substituted corannulene demonstrated by our DFT calculations, and, more recently, confirmed for $C_{20}H_{10-x}(CF_3)_x$ ($x = 2$, 3),[10] allows for the design of molecules with the desired electronic properties. Here, we report the first synthesis, structure, and electronic properties (in solution and in the gas phase) of a derivative of corannulene, which has a higher electron affinity (EA) than the well-studied fullerene electron-acceptor C_{60}.

The reaction of **1** with 35 equivalents of 1,4-$C_4F_8I_2$ at 300 °C led to a pale-yellow crude product, which, according to negative-ion atmospheric pressure chemical ionization (NI-APCI) mass spectrometry, consisted of three major types of molecular species with the general formulas $C_{20}H_4(C_4F_8)_3$, $C_{20}H_4(C_4F_8)_4$, and $C_{20}H_4(C_4F_8)_4(C_4F_8I)$ (see Figure S1 A in the Supporting Information). Subsequent analysis of the crude material by ^{1}H and ^{19}F NMR spectroscopy showed that the starting material **1** was completely consumed, and that the two major products were isomers of C_s-$C_{20}H_4(C_4F_8)_3$ (**2** and **3**, see Scheme 1).

These two compounds were also observed by using HPLC as dominant peaks eluting at 13.5 min (**2**), and 15 min (**3**) (Figure 1). They were isolated with greater than 98 % purity by HPLC separation; the molecular composition was determined using NI-APCI mass spectrometry, as shown in

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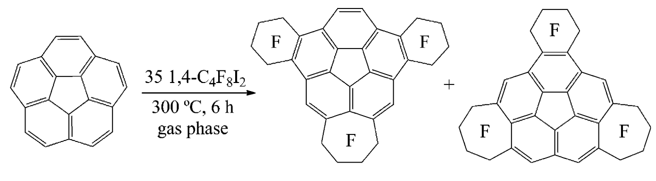

1, C_{5v}-$C_{20}H_{10}$ **2**, C_S-$C_{20}H_4(C_4F_8)_3$-I 15 mol% **3**, C_S-$C_{20}H_4(C_4F_8)_3$-II 5 mol%

Scheme 1. Gas-phase annulation of corannulene.

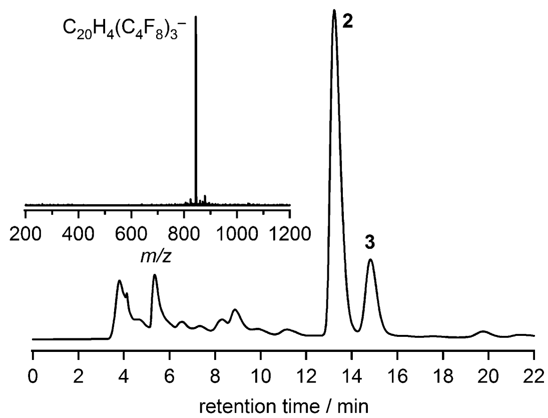

Figure 1. HPLC trace of the crude product formed in the reaction of corannulene with 1,4-$C_4F_8I_2$ (Cosmosil Buckyprep column, 20:80 v/v toluene/*n*-heptane eluent at a flow rate of 5 mL min^{-1}; 300 nm detection wavelength). Inset: NI-APCI mass spectrum of purified **2** (the mass spectrum of **3** is very similar).

Figure 1. Purified **2** and **3** are very pale-yellow solids which are completely stable in the presence of air, they undergo sublimation without degradation, and show good solubility in dichloromethane, chloroform, toluene, and acetonitrile.

The structure of **2** was confirmed by X-ray crystallography.[11] Two perpendicular views of the idealized C_s structure are shown in Figure 2. The C–C distances ($\sigma = 0.003$ Å) and C-C-C angles ($\sigma = 0.2°$) show only minor distortions from those in corannulene itself (e.g. the ranges of the rim C–C bond lengths are 1.379(3)–1.389(3) Å for **2** and 1.378(2)–1.384(2) Å for corannulene[12]). The two C_6F_8 six-membered-ring moieties exhibit cyclohexene-like conformations (see the Supporting Information for more details). The seven-membered C_7F_8 ring exhibits an irregular conformation (see the Supporting Information). The bowl depth of **2**, defined as the average perpendicular displacement of the ten rim C atoms from the least-squares plane of the central pentagon, is 0.783(48) Å (the standard deviation of the ten distances is shown in parentheses; the ten distances range from 0.698 to 0.867 Å). The bowl depths for two independent molecules of corannulene are 0.862(24) and 0.889(16) Å.[12]

Unlike the structures of CORA-2-1[10] and CORA-5-1,[9] molecules of **2** are not packed so that their bowls form a uniform stack. Instead, the only intermolecular π–π interaction shorter than 3.5 Å is between parallel hexagons on the outside surfaces of neighboring molecules (see the Supporting Information). Two C atoms of one hexagon are displaced by 3.32 and 3.45 Å from the least-squares plane of the corresponding hexagon in the other molecule.

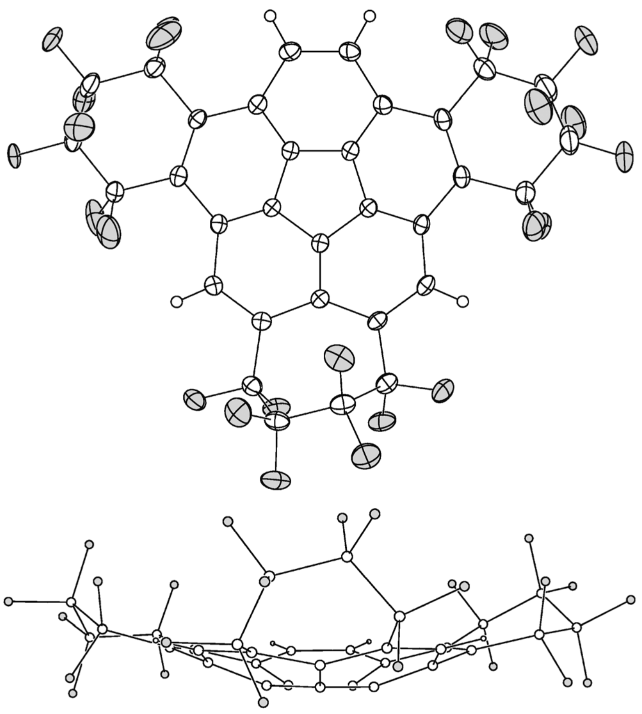

Figure 2. Two views of the structure of **2** (50% probability ellipsoids for non-H atoms are shown in the upper drawing).

Attempts to crystallize **3** did not yield good-quality single crystals, and NMR spectroscopic data do not allow for definitive structure elucidation of this isomer. We therefore performed DFT calculations[13] on compound **2** and the three plausible structures of the other isomer of C_s-$C_{20}H_4(C_4F_8)_3$ (**3**; Figure 3). Compound **2** was found to be the most thermodynamically stable, which is consistent with it being the major product in the crude mixture. Compound **3** is likely to have the structure of the next most stable isomer, namely **B**, which is 17 kJ mol^{-1} higher in energy than **2**, but almost 30 kJ mol^{-1} more stable than the other isomers (Figure 3B). Isomer **B** has

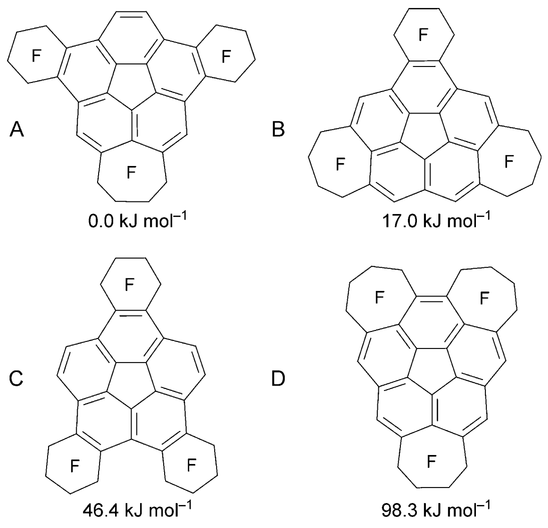

Figure 3. Structures and DFT-calculated relative energies of four possible C_s-$C_{20}H_4(C_4F_8)_3$ molecules.

one cyclohexene ring and two cycloheptene rings, whereas compound **2** has two cyclohexene rings and one cycloheptene ring. There are no close contacts between the rings in the structures of both **2** and **B**, while the close contacts in the higher-energy structures **C** and **D** induce strain in these molecules, and hence this may explain their much higher relative energies and, hence, their absence among the reaction products. Our computational results also indicate that the formation of tetra- as well as pentaannulated corannulenes is highly unlikely (which is confirmed by the experimental data; see Figure S1 in the Supporting Information).

The formation of C_4F_8-annulated corannulene compounds is consistent with radical aromatic substitution of the corannulene core with $I(CF_2)_3CF_2$ radicals formed by thermolysis of 1,4-$C_4F_8I_2$.[14] While formation of a cyclohexene ring was observed before in a reaction of *p*-xylene with 1,4-$C_4F_8I_2$, this study provides the first evidence of the formation of a cycloheptene ring during the reaction of 1,4-$C_4F_8I_2$ with an aromatic substrate. It is notable that an analogous reaction between **1** and 1,4-$C_4F_8Br_2$ proceeds much slower, even when carried out at a higher temperature (360 °C) and for a longer time (30 h). ^{1}H NMR spectroscopic analysis of the product revealed that much of the starting material was unchanged, although APCI mass spectrometric analysis showed that a small amount of $C_{20}H_4(C_4F_8)_3$ was formed (see Figure S1 B in the Supporting Information). We have also explored the reaction of **1** with 1,2-$C_2F_4I_2$ at 300 °C. APCI mass spectrometric analysis of the product showed that up to 12 C_2F_4 fragments were added to the corannulene core (see Figure S1 C in the Supporting Information) and the starting corannulene (**1**) was completely consumed (based on the ^{1}H NMR spectrum, not shown). The ^{1}H NMR spectrum of the product also showed that the ratio between aromatic hydrogen atoms and hydrogen atoms attached to the end of the CF_2CF_2 chain was about 2:1. As a consequence of a likely telomerization of C_2F_4 groups under these reaction conditions (i.e. formation of longer perfluoroalkyl chains), it is difficult to ascertain the average or the highest number of EWGs in the resulting corannulene derivatives. Preliminary HPLC analysis indicated that the isolation of pure compounds would be very time-consuming. Therefore, further optimization of the reaction conditions will be needed in the future.

To get an insight into the effect of the annulation on the electronic properties of corannulene, we measured the gas-phase electron affinity of **2** and its reduction potential in solution. Cyclic and square-wave voltammetry of **2** revealed that the annulation of corannulene by three C_4F_8 chains results in a large 1.23 V shift of the first reversible reduction potential ($E_{1/2}$) of **2** relative to that of **1** in CH_3CN (see Figure 4, top, and the Supporting Information). A direct measurement of the electron affinity of **2** using low-temperature photoelectron spectroscopy (see Figure 4, bottom) resulted in the value of 2.74 ± 0.02 eV, which exceeds the electron affinity of C_{60} (2.689 ± 0.008 eV).[15] The DFT-predicted electron affinity of 2.74 eV for **2** is in excellent agreement with the experimental result. The DFT-predicted electron affinity of the less-abundant isomer **3** (2.65 eV) is lower by 90 meV, which is consistent with the results of square-wave voltammetry (the difference in the SWV first reduction potentials of **2** and **3** is 100 mV, see Table S1 in the Supporting Information). Since the solvation energies of these two similar molecules are not expected to differ, this result shows that the positions of EWGs on corannulene have a significant effect on their electron affinity and reduction potentials. In our earlier study we calculated the electron affinity of one of the isomers of hexasubstituted corannulene $C_{20}H_4(CF_3)_6$ to be 2.53 eV (with a substitution pattern different than **2** and **3**).[9] The lower value may be due to the lower electron-withdrawing ability of CF_3 groups relative to C_4F_8 chains and/or as a result of the difference in the substitution patterns.

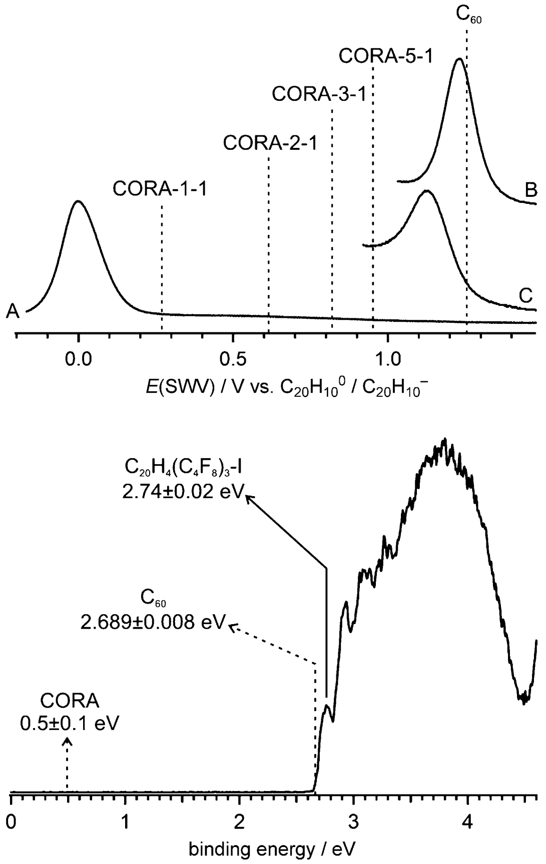

Figure 4. Top: Square-wave voltammetry (SWV) of corannulene $C_{20}H_{10}$ (graph A), C_s-$C_{20}H_4(C_4F_8)_3$-I (**2**; graph B), and C_s-$C_{20}H_4(C_4F_8)_3$-II (**3**; graph C) in $CH_3CN/N(n\mathrm{Bu})_4ClO_4$. Vertical bars denote the reduction potentials of trifluoromethylated corannulene derivatives from Refs. [10] (measured in THF) and [9], the "CORA-X-Y" notation denotes the number of CF_3 groups (X) and the number of the isomer (Y). Bottom: Low-temperature photoelectron spectrum of C_s-$C_{20}H_4(C_4F_8)_3$-I$^-$ ($\mathbf{2}^-$); dashed lines show EAs for CORA[6] and C_{60}.[15]

Interestingly, comparison of the reduction potentials of **2** and C_{60} (1.26 V versus $C_{20}H_{10}^0/C_{20}H_{10}^-$ in acetonitrile) indicates that C_{60} is a slightly stronger acceptor in solution. The reverse order with respect to gas-phase EA values is most likely caused by differences in the solvation energies. Indeed, the DFT-calculated $\Delta\Delta E_{\mathrm{solv}}$ value is -0.90 eV for **2** and -0.96 eV for C_{60} at the same level of theory. This means that the difference between $\Delta E_{1/2}$ and ΔEA should be 0.06 eV, which agrees reasonably well with the experimental value of 0.08 V.

The suitability of these new highly stable and soluble corannulene acceptors for organic electronics will be investigated further, and one relevant feature of their electronic properties is worth mentioning here. Recently Liu and Troisi suggested that the unsurpassed performance of fullerene derivatives as electron acceptors in organic photovoltaics (OPVs), which all have high electron affinities of 2.4–2.8 eV, is rooted in the threefold degenerate LUMO of C_{60}.[16] Although the degeneracy is lifted in derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester($PC_{61}BM$), their LUMO + 1 and LUMO + 2 energies are only slightly higher than their LUMO energy (e.g., 0.07 and 0.15 eV, respectively, for $PC_{61}BM$) and therefore all three orbitals participate in the electron transfer. This drastically increases the rate of the electron transfer in comparison to the acceptors with a "stand-alone" LUMO. From this perspective, fluorine-containing annulated corranulene derivatives can potentially compete with C_{60} derivatives because the twofold degenerate LUMO of $C_{20}H_{10}$ results in a small LUMO/LUMO + 1 gap in derivatives such as **2** and **3** (DFT predicts the LUMO/LUMO + 1 gap in **2** to be 0.16 eV).

In conclusion, the annulation of corannulene in the presence of 1,4-$C_4F_8I_2$ is an efficient and a relatively selective process that yields two main products in which six H atoms are substituted with three C_4F_8 moieties that form six- and seven-membered rings. The major isomer **2** is the first example of a geodesic PAH derivative that is a stronger electron acceptor than the C_{60} fullerene.

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[11] Crystal data for $C_{20}H_4(C_4F_8)_3$-I (**2**): $M_r = 844.35\ \text{g mol}^{-1}$, $P21/n$, $a = 11.9944(9)$, $b = 9.8800(8)$, $c = 23.2268(19)$ Å, $\beta = 93.161(4)$, $V = 2748.3(4)$ Å^3, $Z = 4$, $T = 120(2)$ K, 59235 reflections, 6818 independent reflections, 560 parameters, $R1(I>2\sigma(I)) = 0.0688$, $wR2 = 0.1726$, Bruker APEX-II CCD diffractometer with a Mo-Kα X-ray tube source and graphite monochromator. A semi-empirical absorption correction was applied using SCALE. Refined using SHELXL-97. CCDC 930358 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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