Dehydro[12]- and -[18]Annulenes Fused with Tetrafluorobenzene: Synthesis, Electronic Properties, Packing Structures, and Reactivity in the Solid State

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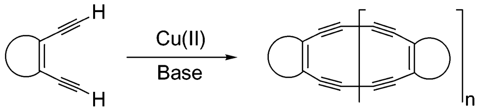
Dehydro[12]- and -[18]annulenes **3** and **4** fused with tetrafluorobenzene were newly synthesized by the copper-mediated oxidative coupling of 1,2-diethynyltetrafluorobenzene. The UV−vis spectra of **3** and **4** showed the maximum absorption to be almost identical to that of the corresponding unsubstituted benzodehydro[12]- and -[18]annulenes **1** and **2**, respectively, while the reduction waves in cyclic voltammetry observed at potentials of −1.48 and −1.56 V vs Fc/Fc$^+$ for **3** and **4** were less negative than those for **1** and **2**. In agreement with these results, theoretical calculations (B3LYP/6-31G(d)) indicated that the HOMO−LUMO gap is similar for **1** and **3** and for **2** and **4** but that the LUMO levels of **3** and **4** are apparently lowered by the electronegative fluorine substituents. The X-ray crystallography of single crystals grown from **3** (crystal A), $\mathbf{3}\cdot C_6H_6$ (crystal B), and a mixture of **1** and **3** (crystal C) demonstrated that the molecules of **3** are stacked in a slanted manner in crystals A and B, while those of **1** and **3** form sandwichlike 1:2 complexes ($\mathbf{3}\cdot\mathbf{1}\cdot\mathbf{3}$) that are stacked in a columnar arrangement in crystal C. Despite the suitable packing for topochemical polymerization, crystals A−C were quite stable against photochemical reaction. In contrast, differential scanning calorimetry showed that the thermal polymerization occurred explosively at 120−135 °C.

Introduction

The chemistry of macrocyclic π-conjugated systems containing acetylenic linkage(s), i.e., dehydroannulenes, has experienced a resurgence in the past decade, and the synthesis and properties of a wide variety of derivatives have been studied.[1] Among these dehydroannulenes, the synthesis of a series of compound types consisting of alkene or arene moieties possessing diyne linkages at adjacent carbons of the unsaturated bond is relatively simple. Such compounds can typically be synthesized[2−12] by the copper-mediated oxidative coupling of ene-diynes or 1,2-diethynylarenes, as depicted in Scheme 1.

SCHEME 1



This method of cyclization was originally applied to the synthesis of the first derivative of this type of dehydroannulene, i.e., dibenzodehydro[12]annulene **1**, which was obtained as the sole isolated product of the reaction.[2] Despite the simplicity of the method, only a few derivatives of this type were reported[3−5] during the first golden age of annulene chemistry between the 1960s and the 1990s when Diederich and co-workers successfully ap-

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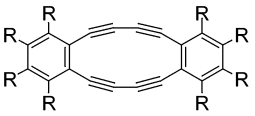
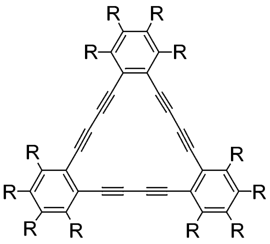
plied this method to the synthesis of a variety of dehydroannulenes with a larger ring size as precursors of cyclo[*n*]carbon.[6a−d] The long blank in the study of this type of dehydroannulenes might be partly attributed to the explosive nature of the highly strained annulene **1** at ambient temperature.[2,9b] A recent X-ray crystallographic study revealed that molecules of **1** form stacked columns in the solid state and that not only the distorted diyne moiety but also the closely packed arrangement of diyne is the cause of the explosive decomposition at room temperature.[9b] It should also be noted that the chemistry of benzo-annelated cyclic polyynes has now developed into a new field related to synthesis of new carbon-rich materials such as graphdiynes.[1c] Tribenzodehydro[18]-annulene **2** was a candidate for the basic unit of graphdiynes, but the synthesis of **2** had long been elusive until its recent achievement by means of a stepwise approach.[13] It has also been reported that the poor solubility of **2** might have been responsible for its elusiveness and that **2** can actually be obtained as a byproduct of the direct cyclization of 1,2-diethynylbenezene.[13b]



R = {H (**1**)
F (**3**)

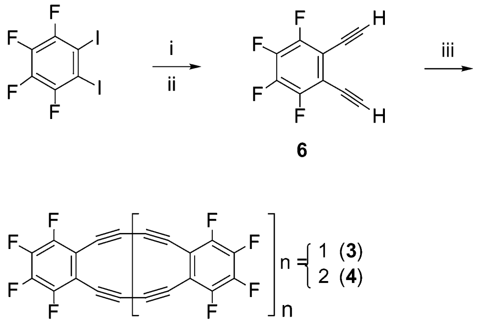


R = {H (**2**)
F (**4**)

In our previous study, a series of dehydroannulenes fused with bicyclo[2.2.2]octene[10a] and 1,4-dimethoxynaphthalene[10b] having diyne linkages were synthesized by the oxidative coupling method shown in Scheme 1, and their spectral properties and redox behavior were investigated together with those of dehydroannulenes having monoyne linkages.[10,14] From these studies, we found that the electron-donating properties of the substituents can significantly modify the electronic properties of the macrocycles, particularly when the annulene π-system is planar. These results interested us in the properties of dehydroannulenes **3** and **4** fused with the electron-withdrawing perfluorobenzene, which were expected to have planar and electron-deficient π-systems.

In the present paper, we describe the synthesis of perfluoro derivatives of dehydro[12]- and -[18]annulenes **3** and **4** and their electronic properties, as studied by electronic spectra, redox potentials, and theoretical calculations. Furthermore, the characteristic packing structure in the solid state controlled by the phenyl/tetrafluorophenyl interaction will be demonstrated. Recently, crystal engineering using the phenyl/pentafluorophenyl interaction has been shown to be useful for the formation of the face-to-face π-stacking structure in the solid state.[15] Also, the photochemical and thermal reactivities of **3** and the face-to-face cocrystals of **3** with **1** and with benzene molecules in the solid state were examined in comparison with the explosive thermal reactivity of **1** at room temperature. [2,9b]

SCHEME 2[a]



[a] Reaction conditions: (i) HC≡CTMS, PdCl$_2$(PPh$_3$)$_2$, CuI, toluene-*i*-Pr$_2$NH; (ii) KOH, H$_2$O−MeOH; (iii) CuCl, TMEDA, O$_2$.

Results and Discussion

Synthesis. For the synthesis of **3** and **4** via the copper-mediated coupling route, preparation of 1,2-diethynyltetrafluorobenzene was required. As shown in Scheme 2, the cross-coupling reaction between trimethylsilylacetylene and 1,2-diiodotetrafluorobenzene under the catalysis of Pd(PPh)$_2$Cl$_2$ and CuI[16] gave 1,2-bis(trimethylsilylethynyl)-3,4,5,6-tetrafluorobenzene (**5**) in 96% yield. Among the two typical desilylation reagents, the use of aqueous KOH in methanol−ether, which allowed completion of reaction in 3 min at room temperature, afforded the diethynylbenzene **6** in 95% crude yield (the formation of diethynyltrifluoroanisole as a byproduct was observed), while the use of tetrabutylammonium fluoride in THF−H$_2$O gave **6** in lower yield (30−50%).

For the cyclization reaction by the copper-mediated oxidative coupling, we used the Swager's condition using Hay catalyst (CuCl−TMEDA−O$_2$ in *o*-dichlorobenzene),[7] and the perfluoro derivatives of dehydroannulenes **3** and **4** were successfully obtained. The products were separated by preparative gel permeation chromatography to give **3** in a yield varying from 20 to 45% and **4** in a yield varying from 10 to 20%. An approximately 5−10% yield of the cyclic tetramer was confirmed on the basis of the APCI-MS and ^{19}F NMR spectroscopy, but its isolation in a pure form was not successful.

Electronic Properties. To compare the electronic properties of perfluorobenzodehydroannulenes **3** and **4** with those of the corresponding benzodehydroannulenes **1** and **2**, UV−vis spectral measurements and cyclic voltammetry (CV) were carried out for **3** and **4**, and the results are shown in Table 1. In the UV−vis measurement, the longest-wavelength absorptions for **3** and **4** were found to be almost identical to those for **1**[2] and **2**,[13a] respectively. These results indicate that the HOMO−LUMO gap of benzodehydro[12]- and -[18]annulenes **1**

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TABLE 1. UV−vis Absorptions, Reduction Potentials, and HOMO and LUMO Levels of 1−4 Calculated at the B3LYP/6-31G(d) Level

compd	$\lambda_{\max}$ (nm)	$E_{\mathrm{pc}}{}^{a}$ (V)^{b}	HOMO (eV)	LUMO (eV)
1	433^{c}	−2.00	−5.44	−2.33
2	369^{d}	−^{e}	−5.60	−2.08
3	435^{f}	−1.48^{g}	−6.15	−3.10
4	372^{f}	−1.56^{g}	−6.31	−2.88

[a] Measured in benzonitrile. [b] V vs Fc/Fc$^+$. [c] In C_6H_6: from ref 2. [d] In CH_2Cl_2: from ref 13a. [e] No redox wave was observed from +1.2 to −2.2 V. [f] In $CHCl_3$. [g] Irreversible cathodic peak.

and **2** is not significantly altered by full substitution with fluorine atoms on the benzene rings. In contrast, the cyclic voltammetry of **3** and **4** in benzonitrile showed the irreversible reduction peak at −1.48 V vs Fc/Fc$^+$ for **3** and at −1.56 V for **4**, while the reversible reduction wave was observed at the more negative potential of −1.9 V ($E_{\mathrm{pc}} = -2.0$ V) for **1** and no redox wave was observed in a range from +1.2 V to −2.2 V for **2** in the same solvent, suggesting that the LUMO levels of **3** and **4** are significantly lowered by the fluorine substituents.

These experimental observations are in good agreement with the results of DFT calculations (B3LYP/6-31G(d)):[17] the calculated HOMO−LUMO gap for **1** agrees well with that for **3**, and similar agreement is observed between those for **2** and **4**, as shown in Table 1. Furthermore, the calculated LUMO levels for **3** and **4** are lower than those for **1** and **2**, respectively, by ca. 0.8 eV due to the electronegative fluorine substituents, which is consistent with the CV measurements.

Packing Behavior of 3 and Cocrystal of 1 and 3. Both the chloroform and benzene solutions of **3** were allowed to evaporate very slowly over 1 week to give single crystals suitable for X-ray crystallographic analysis. In addition, the slow evaporation of a chloroform solution of the 1:1 mixture of **1** and **3** gave a cocrystal of **1** and **3**. By a similar procedure, an attempt was made to obtain a single crystal of **4** and a cocrystal of **4** and **2**.[13b] Unfortunately, however, no crystals obtained in these attempts were suitable for X-ray crystallography. Thus, only a series of structures of the single crystals of **3** and the cocrystal of **1** and **3** were determined by X-ray crystallography.

As shown in Figure 1a, a single crystal obtained from the chloroform solution (crystal A) was found to consist of only **3**, and it was packed in a parallel and slanted arrangement with a distance d between the centers of the annulene cores of 4.99 Å and an angle Φ between the plane of the core and the stacking axis of 39°. In the stacked structure, one of the tetrafluorobenzene rings in **3** faces the annulene core of another molecule of **3**, while the other tetrafluorobenzene ring is free from intermolecular stacking. This slanted arrangement in the packing of **3** is different from the crystal structure of **1**, which was found to be packed in a columnar arrangement. To examine the possible intermolecular electrostatic interaction, the Mulliken charge was calculated for **3** using B3LYP/6-31G(d). As expected from the electronegativity of fluorine atoms, the carbon atoms in the tetrafluorobenzene ring were positively charged (+0.28, +0.26, +0.02) and the adjacent sp carbon was found to be the most negatively charged (−0.38), while the next sp carbon near the center of the molecule was the most positively charged (+0.34). When the calculated charge distribution is depicted in the stacked structure of crystal A (Figure 1b), the electrostatic repulsion between the tetrafluorobenzene ring and the annulene core appears to be minimized in the slanted packing. Thus, the possible electrostatic interaction between the fluorobenzene ring and the annulene core could be playing an important role in the slanted packing. A similar stacking of hexafluorobenzene and the annulene core of **1** has also been reported.[9b]

On the other hand, a single crystal obtained from the benzene solution (Figure 1c, crystal B) was found to contain **3** and a benzene molecule in a 1:1 ratio. In this case, the packing behavior of **3** resembled that in crystal A, except that the benzene molecule faced one of the tetrafluorobenzene rings in **3** that was free in crystal A. This extra stacking with benzene brings about not only a favorable face-to-face benzene/tetrafluorophenyl interaction but also a filling of the free space in crystal A. Apparently, the benzene molecule slightly pushes **3** to make the stack more slanted so that the distance d (6.35 Å) and the angle Φ (26°) become longer and narrower, respectively. This change appears to induce an unfavorable electrostatic repulsion between the annulene core and the tetrafluorobenzene moiety, as depicted in Figure 1d, but the instability caused by such an electrostatic repulsion can be compensated for by the favorable benzene/tetrafluorophenyl interaction and space filling, as described above.

In crystal C, obtained from the chloroform solution of a 1:1 mixture of **1** and **3**, a face-to-face alternate stacking pattern of **1** and **3** was expected, as in the case of cocrystals having a phenyl/perfluorophenyl interaction.[15] However, the result of X-ray crystallography disclosed an unexpected packing pattern of **1** and **3** in a 1:2 ratio, in which a sandwichlike complex **3·1·3** was formed, and these units were stacked in a columnar arrangement, as shown in Figure 2. The angles, Φ_1, Φ_2, and Φ_3, were 78°, 79°, and 75°, respectively, and the distances, d_1, d_2, and d_3, were 3.69, 3.69, and 3.87 Å, respectively, indicating that the difference in stacking pattern for **3·1** and **3·3** is quite small. In the stacking of this sandwichlike complex, the polar-π phenyl/perfluorophenyl attractive interaction[15c] appears to play a dominant role. In addition, there may be some charge-transfer interaction, although it should be very small judging from the redox properties of **1** and **3** and from the lack of a charge-transfer band in solution. The two ends of the dibenzodehydro[12]annulene framework of **3** are bent slightly outward (or the central part is bent slightly inward), as shown in Figure 2b. It should be noted that the sandwichlike units form a highly ordered columnar stack, although the exact reason for

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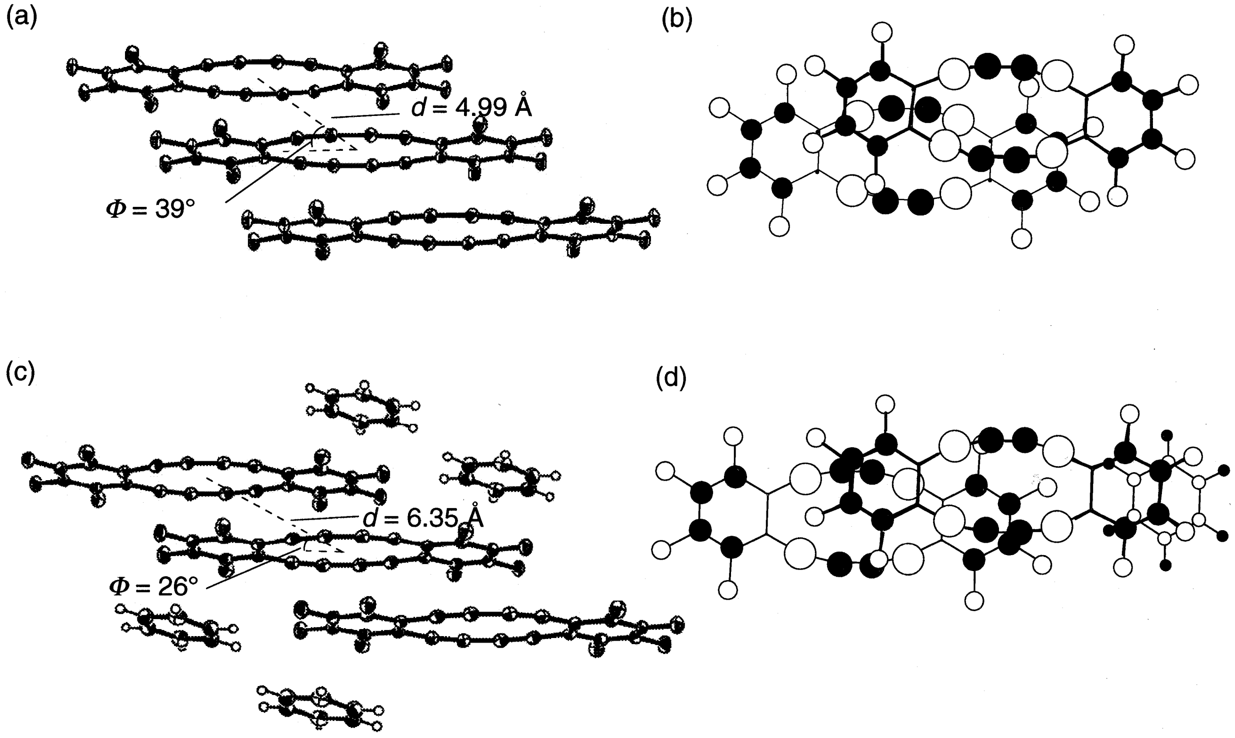

FIGURE 1. ORTEP drawings showing the stacking structure of (a) crystal A and (c) crystal B, and sketches with the Mulliken charge of (b) **3** and (d) **3**·C_6H_6 calculated at the B3LYP/6-31G(d) level: light and dark colors indicate negatively and positively charged atoms, respectively; the diameters of the circles are in proportion to the values of charge distribution.

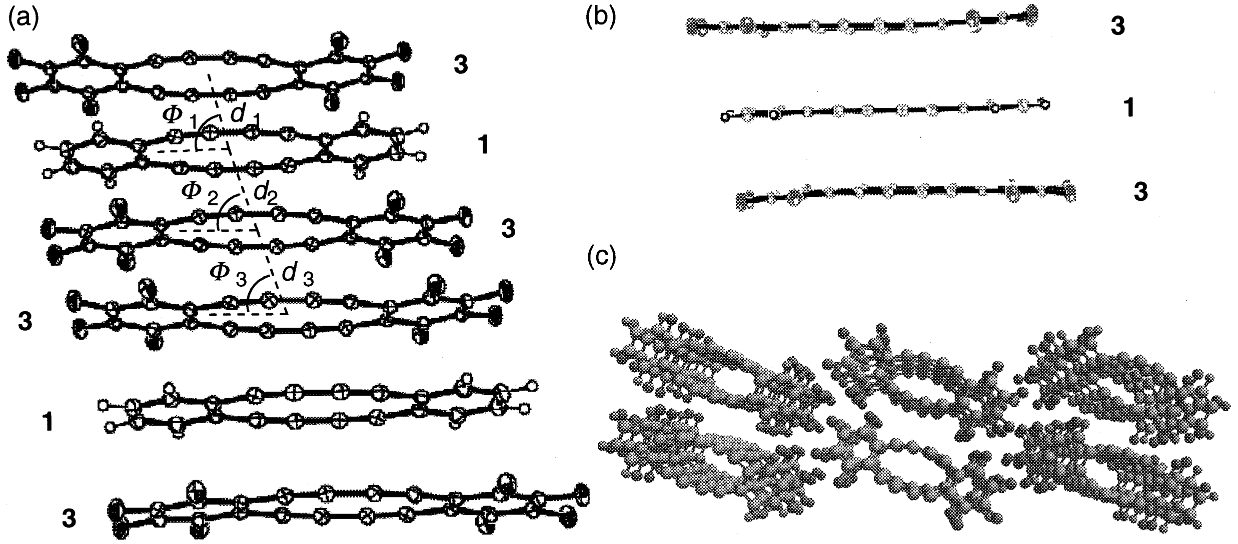

FIGURE 2. (a) ORTEP drawings showing the stacking structure of crystal C (**3**·**1**·**3**). (b) Side view of the sandwich complex **3**·**1**·**3**. (c) Packing mode of the crystal C.

this stacking of the sandwichlike units is not entirely clear at present. However, the possible electrostatic interaction between two molecules of **3** as observed in crystal A would be reduced by complexation with **1**. Attempts were made to obtain the cocrystal of **1** and **3** in a different ratio by using solutions made from mixtures of **1** and **3** in various ratios, but no other type of cocrystal could be obtained.

Reactivity in the Solid State. To study the relation between reactivity and the packing mode in the solid state of the perfluorobenzodehydro[12]annulene with strained butadiyne linkages, crystals A−C were subjected to photoirradiation and a thermal reaction. By the photoirradiation of butadiyne derivatives, topochemical polymerization has been shown to proceed in the solid state.[15a,18−20] As a prerequisite for such topochemical photopolymerization, an intermolecular distance d of approximately 5 Å and a stacking angle Φ of approximately 45° are required for trans polymerization,[15a,18,19] and a d of approximately 3.5 Å and Φ of approximately 90° are required for cis polymerization.[15a]

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SCHEME 3

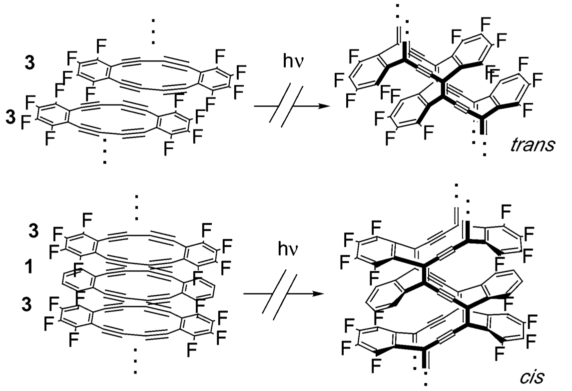

TABLE 2. DSC Data for Crystals A−C and 4

compd	T_{onset} (°C)	$T_{\max}$ (°C)	$w^{1/2}$ (°C)	Δ*H* (kcal/mol)
3 (A)	100	120	9	265
3·C_6H_6 (B)	100	135	5	245
3·1·3 (C)	113	132, 136[a]	3, 3	227
4	193	221	13	209

[a] Two peaks were observed.

The packing in crystals A and C appears to satisfy these prerequisites for the trans and cis polymerizations, respectively. However, despite the presence of strained butadiyne linkages, crystals A and C as well as B were found to be quite inert against photoirradiation: no reaction was observed for these crystals upon irradiation with a high-pressure or low-pressure mercury lamp for several days (Scheme 3).

Next, differential scanning calorimetry (DSC) was performed to study the thermally induced exothermic reaction. There have been several recent reports of the exothermic polymerization of benzodehydroannulenes,[21,22] including **1**[21b] and its derivatives.[7] Interestingly, the products of these thermal reactions of various benzodehydroannulenes were shown to contain some carbon-rich materials such as “bucky tubes” and “bucky onions”,[21] as well as a material with a novel polyacetylene tube structure formed by topochemical polymerization.[20]

As shown in Table 2, the DSC analysis indicated that irreversible exothermic transitions take place for crystals A−C at 120−136 °C with Δ*H* of 227−265 kcal/mol. In the case of crystal C, two peaks appeared in the exotherm, suggesting that the reaction proceeds in two steps. These exothermic transition temperatures were in the same range (120−136 °C) but were slightly higher than that for the tetraalkyl and tetraalkoxy derivatives of **1** (100−125 °C).[7] Also, these temperatures for crystals A−C were considerably higher than that for **1** without a substituent, which showed thermal instability even at ambient temperature. The relatively higher transition temperatures reported for the tetraalkyl and tetraalkoxy derivatives of **1** in comparison with that for **1** were attributed to the difference in packing pattern; the reactive diyne moieties of **1** are packed closely,[9b] while those of the others are separated due to the presence of substituents.[7] In the case of crystals A−C, the reactive diyne moieties are closely located and, especially for crystal C, columnar stacking similar to the one observed in **1** was shown to be present. Rather higher transition temperatures were observed for crystals A−C despite such crystal structures, which may suggest that the electron deficiency in the [12]annulene's π-conjugated system in **3** has a reduced thermal reactivity. DSC analysis of **4** recrystallized from chloroform was also carried out and showed a sharp exotherm at 221 °C with Δ*H* of 209 kcal/mol. In this case, the transition temperature was lower than the value reported for **2** (232 °C).[22b] Due to the lack of packing information for compounds **2** and **4**, we cannot provide a detailed discussion of this phenomenon, but it is to be noted that the difference in transition temperatures between **2** and **4** was found to be much smaller than that between **1** and **3**.

After these DSC measurements as well as independent experiments of the explosion under vacuum, all of the yellow crystals A−C and **4** turned to black materials that were insoluble in any organic solvent. Judging from the lack of peaks for oligomeric products of **2** and **4** in MALDI-TOF MS spectra, the black products do not seem to be topochemical polymers but rather are likely carbon-rich materials such as amorphous carbon, graphite, and so on, as have been observed for other thermal products of benzodehydroannulenes.[21,22]

Conclusion

The perfluoro derivatives of dibenzodehydro[12]annulene **3** and tribenzodehydro[18]annulene **4** were synthesized through the use of copper-mediated oxidative cyclization of 1,2-diethynyltetrafluorobenzene. These annulenes were characterized by an electron-deficient π-conjugated system, as compared with the corresponding annulenes **1** and **2**, as shown by electrochemical measurements and theoretical calculations. The structures of single crystals containing **3** were determined by X-ray analysis and indicated that packing behavior is controlled by the phenyl/tetrafluorophenyl interaction. However, even though the stacked structures desirable for topochemical polymerization were constructed in crystals of **3**, **3**·C_6H_6, and **3·1·3**, such polymerization did not proceed upon photoirradiation, possibly due to the expected instability of the topochemical products. In contrast, for these crystals **3**, **3**·C_6H_6, and **3·1·3** (crystals A−C), the explosive thermal polymerization took place at a relatively higher temperature compared with the dehydroannulene crystals having no fluorine substituent, despite the close location of the diyne units. These results seem to imply that the electron-withdrawing fluorine substituents reduce the reactivity of the highly strained [12]annulene core.

Experimental Section

General. Toluene was distilled from sodium benzophenone ketyl. Diisopropylamine was distilled over CaH_2. All other solvents and reagents were used as purchased. The chemical

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shifts of NMR measurements are referenced to the internal $CDCl_3$ (δ 7.26 in ^{1}H NMR and δ 77.0 in ^{13}C NMR) or C_7D_8 (δ 20.4 (CD_3) in ^{13}C NMR) and the external $CFCl_3$ for ^{19}F NMR. Preparative gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns. DSC analyses was performed with the elevation rate of 4 °C/min. Theoretical calculations were performed using the Gaussian 98 program.[17]

Benzodehydro[12]- and -[18]Annulenes 1 and 2. The oxidative cyclization of 1,2-diethynylbenzene[23] (520 mg, 4.12 mmol) was performed according to the literature procedure.[13b] The separation of the crude mixture was performed by preparative GPC to give **1** (33 mg, 0.13 mmol, 6%) and **2** (157 mg, 0.42 mmol, 30%).

1,2-Bis(trimethylsilylethynyl)-3,4,5,6-tetrafluorobenzene (5). To a degassed solution of 1,2-diiodotetrafluorobenzene (2.00 g, 4.98 mmol), $Pd(PPh_3)_2Cl_2$ (0.176 g, 0.251 mmol), CuI (0.153 g, 0.803 mmol), and dry diisopropylamine (1.4 mL) in toluene (60 mL) was added trimethylsilylacetylene (1.76 mL, 1.22 g, 12.5 mmol), and the reaction mixture was stirred at 60 °C for 20 h under an argon atmosphere. The reaction was quenched with water, and the mixture was extracted with ether, washed with aqueous NaCl, and dried over $MgSO_4$. After the removal of the solvent and the volatile under reduced pressure, the crude product was purified with column chromatography over silica gel eluted with hexane to give **5** (1.64 g, 4.79 mmol, 96%) as a colorless solid: mp (DSC) 118.2−119.2 °C; IR (KBr) 2163 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.29 (s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 148.3 (m), 140.8 (m), 111.4 (m), 107.4 (s), 92.8 (s), −0.3 (s); ^{19}F NMR (282.4 MHz, CD Cl_3) δ −14.7 (d, J = 17 Hz), −34.1 (d, J = 17 Hz). Anal. Calcd for $C_{16}H_{18}F_4Si_2$: C, 56.11; H, 5.30. Found: C, 56.18; H, 5.11.

Perfluorobenzodehydro[12]- and -[18]Annulenes 3 and 4. A solution of KOH (ca. 500 mg) in distilled water (2 mL) was added in one portion to a solution of **5** (913 mg, 2.67 mmol) in methanol (45 mL) and ether (9 mL). The reaction mixture was vigorously stirred at room temperature for 3 min; the reaction was quenched quickly with water (10 mL), and the mixture was extracted with pentane and dried over $MgSO_4$. The solvent was evaporated carefully with a cold bath (ca. 10 °C) to give crude **6** (490 mg, 2.47 mmol, 93%) as a colorless solid: mp (DSC) 36.0−38.0 °C; IR (KBr) 2120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 148.8 (m), 141.2 (m), 110.6 (m), 88.7 (s), 72.4 (s); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −14.3 (d, J = 17 Hz), −32.9 (d, J = 12 Hz); EI MS m/z 198 (M^+). To prevent loss by sublimation, the crude **6** was used in the next step without further purification. A solution of CuCl (309 mg, 3.11 mmol) and TMEDA (19 mL) in *o*-dichlorobenzene (200 mL) was saturated with O_2 by bubbling through the solution. Then a solution of **6** (490 mg, 2.47 mmol) in *o*-dichlorobenzene (200 mL) was added dropwise over a period of 1 h. The mixture was stirred for 5 h with O_2 bubbling and overnight under air. The reaction was quenched by 200 mL of 0.5 N HCl, and the organic layer was extracted with $CHCl_3$, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. The combined organic layer was evaporated under reduced pressure (ca. 20 mmHg) to remove $CHCl_3$ and at ca. 0.1 mmHg with heating by a hot bath (ca. 60 °C) to remove *o*-dichlorobenzene. The crude mixture was separated with preparative GPC to give crude **3** (233 mg, 0.59 mmol, 48%) and **4** (78.2 mg, 0.13 mmol,16%). The separated products were recrystallized from $CHCl_3$ for **3** and from C_6H_6 for **4** to give pure **3** and **4** as yellow crystals. **3**: mp (explosive decomposition at 120 °C); IR (KBr) 2198, 2133 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 435 (3.15), 399 (3.35), 372 (4.37), 361 (3.96), 352 (4.00), 345 (4.04), 298 (4.91), 280 (4.69), 265 (4.25) nm; ^{13}C NMR (75.5 MHz, C_7D_8) δ 147.1 (m), 142.5 (m), 115.4 (m), 89.2 (s), 86.0 (s); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −9.7 (d, J = 17 Hz), −30.1 (d, J = 12 Hz); HRMS (EI) calcd for $C_{20}F_8$ 391.9872, found 391.9864. **4**: mp (explosive decomposition at 221 °C); IR (KBr) 2157 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 372 (4.66), 363 (4.54), 339 (4.97), 327 (4.90), 308 (4.70), 288 (4.41), 282 (4.40); ^{13}C NMR (75.5 MHz, C_7D_8) δ 149.7 (m), 142.2 (m), 111.0 (m), 84.1 (s), 74.4 (s); ^{19}F NMR (282.4 MHz, CD Cl_3) δ −11.6 (d, J = 17 Hz), −29.5 (d, J = 12 Hz); HRMS (FAB) calcd for $C_{30}F_{12}$ 587.9808, found 587.9790.

Cyclic Voltammetry. The cyclic voltammetry (CV) cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out for 1.0 mM solutions of each sample with tetrabutylammonium perchlorate as a supporting electrolyte (0.1 M) in benzonitrile, and the values for reduction potentials were calibrated with ferrocene as an internal standard.

X-ray Structural Determination. The intensity data were collected with a CCD area detector with graphite monochromated Mo Kα radiation. Frames corresponding to an arbitrary hemisphere of data were collected at −150 °C using ω scans of 0.3° counted for a total of 10 s per frame. The structures were solved using the Bruker SHELXTL program package. Crystallographic data are given in Supporting Information.

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Supporting Information Available: ^{19}F NMR spectra of **3** and **4**, ^{13}C NMR spectra of **6**, X-ray crystallographic data for crystals A−C, and Cartesian coordinates and total energies for the optimized structures of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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