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Stereochemical Investigation of the Products of the Photoinduced Perfluoroalkylation−Dimerization of Anthracene

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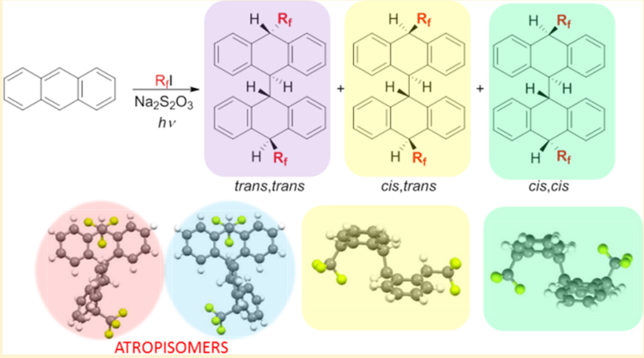
S *Supporting Information*



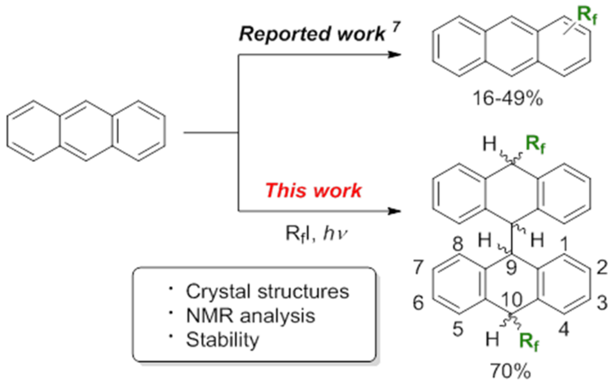
ABSTRACT: The photoinduced perfluoroalkylation of anthracene has been shown to provide 9,9′,10,10′-tetrahydro-10,10′-diperfluoroalkyl-9,9′-bianthracenes in over 70% yields, each perfluoroalkyl iodide producing three diastereomers. The structures of all three diastereomers (*cis,cis*, *cis,trans*, and *trans,trans* isomers) have been elucidated by both NMR and X-ray crystallographic analyses. Most notably, an X-ray crystallographic analysis has revealed that the *trans,trans* diastereomer having the two trifluoromethyl groups in 10,10′-positions adopts a 74° twisted relationship of the two dihydroanthracene rings. Furthermore, each of the two *trans,trans* isomers **2a**,**b** has been shown to exist as a mixture of new types of atropisomers and the energy barrier for the interconversion of the two atropisomers has been estimated to be 12 kcal/mol by variable-temperature NMR analysis.

■ INTRODUCTION

Anthracene derivatives are an important class of compounds that have been widely used as organic semiconductors, organic electroluminescence materials, and fluorogenic dyes.[1] A number of synthetic approaches are available to access these compounds using anthracene as the starting building block. The majority of the synthetic reactions involve the central ring of anthracene by taking advantages of the high electron density and the specific π conjugation at C-9 and C-10 of anthracene, as in the case of [4 + 2][2] and [4 + 4][3] electrocyclic reactions, Friedel−Crafts reactions,[4] and oxidation to quinone.[5] However, there have been only a few examples reported on other types of direct C−C bond forming reactions involving the C-9/C-10 positions of anthracene.[6] In this context, we have been attracted to the notion that the strongly electron-deficient perfluoroalkyl (R_f) radicals would readily undergo reactions on the electron-rich central ring of anthracene. There have only been a limited number of such transformations reported[7] where the reaction proceeds by a perfluoroalkyl radical addition followed by rearomatization to produce perfluoroalkylated anthracenes. However, these reactions proceed in a relatively low chemical yield and often without high regioselectivity (Scheme 1).

We have previously shown that perfluoroalkyl radicals generated by UV irradiation undergo efficient addition reactions to olefins in the presence of $Na_2S_2O_3$.[8] However, the use of anthracene under our photochemical conditions with a perfluoroalkyl iodide resulted in the formation of the perfluoroalkylation−dimerization product 9,9′,10,10′-tetrahydro-10,10′-bis(perfluoroalkyl)-9,9′-bianthracene (**2**), as a mixture of three diastereomers instead of perfluoroalkylated anthracene[9] (Scheme 1). There have been several reports[10] on radical reactions generating the 9,9′-disubstituted 9,9′,10,10′-tetrahydrobianthryl framework. Waters demonstrated that methyl, phenyl and benzyl radicals add to anthracene to give the corresponding 10,10′-disubstituted 9,9′,10,10′-tetrahydro-9,9′-bianthracenes.[10b−d] However, these reactions proceeded only in low yields (6−23% yield). Bickel and Kooyman[10a] and

Scheme 1. Radical Perfluoroalkylation of Anthracene



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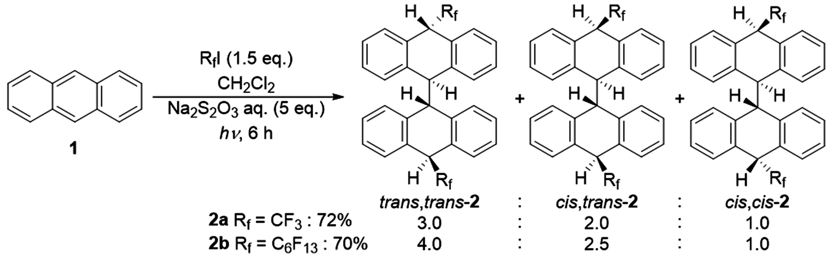
Scheme 2. Perfluoroalkylation of Anthracene



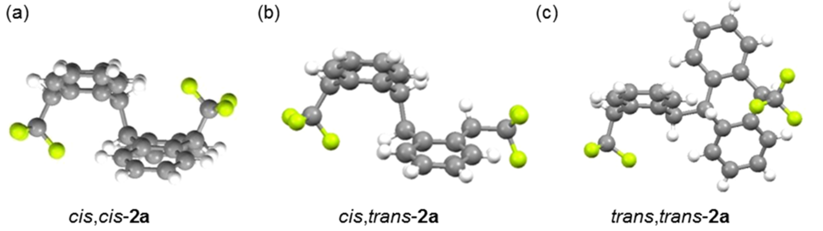


Figure 1. Crystal structures of compound **2a**: (a) *cis,cis*-**2a**; (b) *cis,trans*-**2a**; (c) *trans,trans*-**2a**. Color code: yellow-green, F; gray, C; white, H.

Tokura[10e] have independently reported that the radical reaction of anthracene mediated by α,α'-azobis(isobutyronitrile) (AIBN) furnished 10,10′-bis(2-cyano-2-propyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene. Moreover, nitrogen dioxide addition to anthracene was studied by Kaupp[10g] to produce the corresponding 10,10′-dinitro derivatives; these products were obtained in low yields and their stereochemistry was not assigned. Sigman[10f] reported that the UV irradiation of anthracene in water gave a mixture of three diastereomers of 9,9′-dihydroxylated products, of which the stereostructure of only the *trans,trans* isomer was determined by X-ray crystallographic analysis.

We wish to report herein that (1) the addition of photochemically generated electron-deficient R_f radicals to anthracene results in the formation of a diastereomeric mixture of the bis-perfluoroalkylated anthracene dimer 9,9′,10,10′-tetrahydro-10,10′-bis(perfluoroalkyl)-9,9′-bianthracene (**2**) in high yields, (2) the stereostructures of all three diastereomers obtained have been determined unambiguously by both NMR and X-ray crystallographic analyses, and (3) the *trans,trans* diastereomers of both **2a** and **2b** exist as a mixture of new types of atropisomers and their interconversion energy barrier has been estimated.

■ RESULTS AND DISCUSSION

Radical reactions of trifluoromethyl and perfluororohexyl iodides with anthracene (**1**) were performed in the presence of $Na_2S_2O_3$ under UV irradiation in a $CH_2Cl_2-H_2O$ mixed solvent, which gave a diastereomeric mixture of R_f-incorporated dimeric products **2a**,**b** respectively, both in good yields (Scheme 2). Although the reaction was performed in the presence of water,[10f] the hydroxyl-substituted products were not observed in our reaction. This may be because the perfluoroalkyl radical is formed more quickly from the iodide precursor in comparison to an electron transfer to generate the radical cation from anthracene[10f] or other cationic species, thus suppressing the nucleophilic addition of water to the radical cation or cations. Dimeric **2** was found to consist of three stereoisomers (*cis,cis*-, *cis,trans*-, and *trans,trans*-**2**) originating from the configuration of the two central cyclohexadiene rings, and their isomeric ratios were determined by the integration of ^1H NMR peaks. The *trans,trans* isomer was produced as the major product in both cases. The stereoisomer *trans,trans*-**2** was isolated by silica gel column chromatography. However, the isolation of *cis,cis*-**2** and *cis,trans*-**2** proved difficult, and only a small amount of each of the pure diastereomers was obtained by recrystallization.

Then X-ray crystal structure analysis was performed for the determination of the stereostructures of the trifluoromethylated dimer **2a** (Figure 1).

In all isomers, each central cyclohexadiene ring adopts a flattened boatlike conformation in order to minimize the steric repulsions between the otherwise juxtaposed peri hydrogen atoms.[11] Both trifluoromethyl groups of *cis,cis*- and *trans,trans*-**2a** are oriented in pseudoaxial positions.[12] However, one of the two trifluoromethyl groups was observed to adopt a pseudoequatorial position for *cis,trans*-**2a**. Furthermore, the 9,9′-hydrogens of *cis,cis*- and *cis,trans*-**2a** were oriented in pseudoequatorial positions, thus constituting the C_2-symmetric structure of the bis(9,10-dihydroanthracene) moiety. In contrast, the two 9,10-dihydroanthracene rings of *trans,trans*-**2a** were found to be twisted around C-9−C-9′ bond by 74°. The C-9−C-9′ bond lengths of *cis,cis*-**2a**, *cis,trans*-**2a**, and *trans,trans*-**2a** were determined to be 158.5, 158.2, and 154.1 pm, respectively. The distances of the first two isomers are longer than that of a standard $C(sp^3)-C(sp^3)$ bond (154 pm for ethane), presumably to alleviate the steric congestion; the F⋯H-9 distances of *cis,cis*- and *cis,trans*-**2a** are found to be 230.4 and 227.4 pm, respectively.

The space group of *trans,trans*-**2a** was determined to be $P2_12_12_1$, and a racemic crystal was observed (Figure 2). Thus, this isomer has hitherto unknown atropisomeric chirality with the axis along the linking C-9−C-9′ bond of the two 9,10-dihydroanthracene rings. Two enantiomers were assigned as *S* (left in Figure 2) and *R* (right) on the basis of the Cahn−Ingold−Prelog rules.[13,14] Thus, viewing the structure along the chiral C-9−C-9′ axis and applying the same rule for axially chiral compounds of the preference of closer groups rather than farther ones, the front CF_3 group (shown in red in Figure 2c) should be the highest priority and the hydrogen atom on the front (blue) next. Then the absolute configuration of the

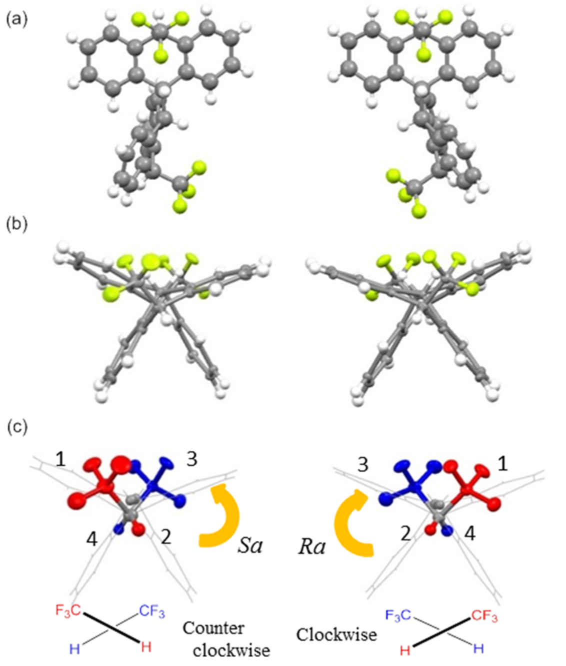


Figure 2. X-ray structure of *trans,trans*-**2a**: (a) top view of one dihydroanthracene ring; (b) top view along the axis; (c) assignment of absolute configurations of atropisomers. The left section shows the *Sa* form, and the right section shows the *Ra* form.

isomer on the left side of Figure 2 was assigned as *Sa* and the right as *Ra*.

The highly symmetrical conformational structures of both *cis,cis* and *cis,trans* isomers are clearly manifested in their NMR spectra and are in line with their crystallographic structures, suggesting the virtually identical three-dimensional structures both in solution and in the crystal form. It is interesting to note that the NMR spectra of these isomers of trifluoromethylated and perfluorohexylated compounds **2a,b** resembled each other, possibly reflecting the highly significant repulsive interactions between the two 9,10-dihydroanthracene ring systems (see the Supporting Information). However, the NMR spectral patterns observed at 296 K of the other diastereomers, *trans,trans*-**2a** and *trans,trans*-**2b**, were quite different (see Figure 3). In the case of *trans,trans*-**2b**, observation of the nonequivalent aromatic protons seems to support the structure obtained by its X-ray analysis. In contrast, *trans,trans*-**2a** showed dissimilar broad ^{1}H signals in the aromatic region. Our low-temperature proton NMR study for *trans,trans*-**2a** demonstrated that, while relatively broadened proton peaks were observed at temperatures between 296 and 243 K, all aromatic hydrogen signals were separated completely at 233 K and showed almost the same spectrum as that obtained for *trans,trans*-**2b** at 296 K. The broad NMR signals of *trans,trans*-**2a** might be the result of the rapid ring inversion of the cyclohexadiene ring[11] or relatively facile rotation around the C-9−C-9′ bond. A variable-temperature (VT) NMR experiment was then undertaken in an effort to assess the rotational energy barrier around the C-9−C-9′ bond as well as the ring inversion barrier of the cyclohexadiene ring. The results of the VT experiment showed that the energy barrier could be estimated to be 12 kcal/mol. Furthermore, we had expected that *trans,trans*-**2b** should show a conformational transition at high temperature, as was observed with *trans,trans*-**2a** at 243 K. However, even at 393 K there was very little merging movement of the aromatic proton signal. Thus, the energy barrier for both the restricted rotation of the 9,10-dihydroanthracene ring and the cyclohexadiene ring inversion should be estimated as >19.7 kcal/mol.

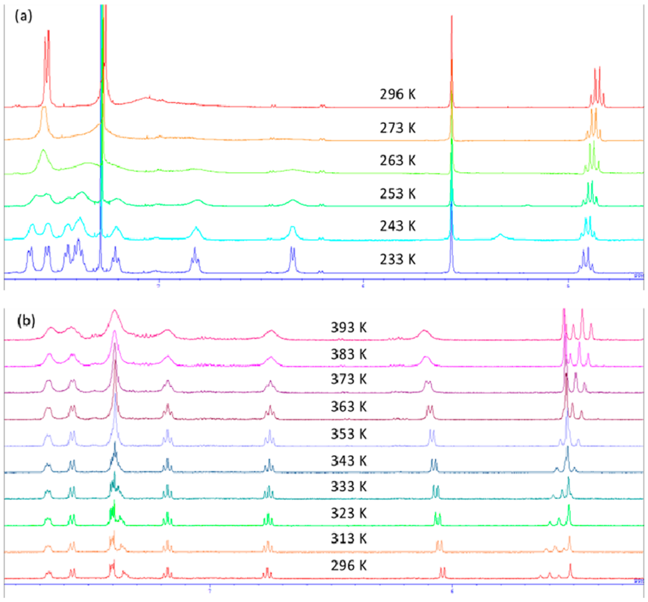


Figure 3. 500 MHz VT ^{1}H NMR spectra of (a) *trans,trans*-**2a** in $CDCl_3$ and (b) *trans,trans*-**2b** in DMSO-d_6.

To determine which of these two processes bears the lower energy barrier, quantum-chemical calculations of *trans,trans*-**2a** were performed.

The energy optimization was carried out for the two types of *trans,trans*-**2a** with two CF_3 groups in the axial positions, as observed in the X-ray structure, or the equatorial positions. Figure 4 shows the optimized geometry of the two types of *trans,trans*-**2a**. The calculation showed that the former with a 67.5° H−C-9−C-9′−H dihedral angle is energetically more stable by 3.3 kcal/mol at the B3LYP/6-31+G* level of theory than the latter with a completely antiperiplanar relationship between these two C−H bonds. This energy difference may stem from the difference in the close contacts of a fluorine atom with the hydrogen at the peri position. Thus, the shortest H···F distance in the former case was 237.1 pm for F···H-9 (the sum of their van der Waals radii being 267 pm) and 290.1 (F···H-1) and 291.7 (F···H-8) pm. Because of the symmetry of the structure, these contacts were recognized for both sides. However, 232.6 and 259.7 pm for F···H-1 and F···H-8 (four contacts in each case) should result in a more unfavorable scenario, thereby resulting in the higher stability for the conformer with two CF_3 groups in the pseudoaxial positions. Substitution of the F atom in the CF_3 group for C_5F_{11} in *trans,trans*-**2a** with axial CF_3 groups should increase the above repulsive interaction with either the other ring or a peri

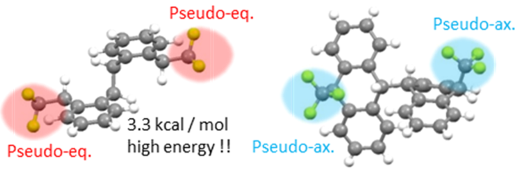


Figure 4. Optimized structures of two *trans,trans*-**2a** conformers.

hydrogen atom, and thus, the easier rotation around the C-9—C-9′ bond axis would become possible, as was observed by the variable-temperature NMR study (Figure 3).

Similar to our case, the structure of a dimerized 9,9′-dihydroanthracene having a bulky silyl substituent in the 10,10′-positions was reported to adopt the twisted conformation by Kako and Nakadaira.[12d] In spite of crystallographic confirmation of this compound as a racemic crystal, such a phenomenon was not discussed at all. In addition, Harvey[12a] postulated that two *tert*-butyl groups in these positions would prefer a twisted structure on the basis of their ^{1}H NMR analysis. In contrast, the X-ray structure of the dimerized dihydroanthracene having two less bulky hydroxyl groups in the 10,10′-positions has been reported and clarified;[10f] these OH moieties were found to orient in the pseudoequatorial positions and neither of the dihydroanthracene rings showed the twisted structure. Harvey[12a] also predicted the structure of the *cis,trans* isomer with both substituents in pseudoaxial positions, which is in sharp contrast with our case. Presumably, significantly sterically bulky groups such as *tert*-butyl groups (*A* value 4.7—4.9 kcal/mol) does not allow them to fit in the pseudoequatorial positions, whereas this was not the case for the much smaller CF_3 substituent (*A* value 2.4—2.5 kcal/mol).[15]

In summary, we found that the photoradical reactions of anthracene using trifluoromethyl or perfluorohexyl iodides as radical precursors smoothly furnished 9,9′,10,10′-tetrahydro-10,10′-diperfluoroalkyl-9,9′-bianthracenes in high yields which were found to consist of three different stereoisomers (*cis,cis*, *cis,trans*, and *trans,trans* forms) due to the linkage of the two central cyclohexadiene rings. Furthermore, we successfully obtained the details of crystal structures of all of these stereoisomers by X-ray analysis. Especially interesting were that (1) the two dihydroanthracene ring systems of the *trans,trans* diastereomers **2a**,**b** are twisted by 74° around the C-9—C-9′ bond and (2) the racemic crystals of *trans,trans*-**2a** were obtained as a mixture of new types of atropisomers. In addition, NMR analysis as well as quantum chemical calculations led to the unequivocal expectation that *trans,trans*-**2a** underwent ring inversion of the cyclohexadiene ring and free rotation around the C-9—C-9′ bond in solution was found to stop at temperatures as low as 233 K. Attempts to separate the two axially chiral atropisomers of *trans,trans*-**2a** are currently ongoing in our laboratory. The mechanistic details of this photoinduced radical reaction will be explored further.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed with a high-pressure Hg lamp (Ushio, 450 W). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a 400 MHz (399.8 MHz for ^{1}H, 100.5 MHz for ^{13}C, and 376.2 MHz for ^{19}F) or 500 MHz (500.16 MHz for ^{1}H, 125.8 MHz for ^{13}C, and 470.6 MHz for ^{19}F) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (δ 0.00 ppm for ^{1}H), chloroform-*d* ($CDCl_3$: δ 76.9 ppm for ^{13}C), and trichlorofluoromethane ($CFCl_3$: 0.00 ppm for ^{19}F) as internal standards unless otherwise noted. Crystallographic data were collected with graphite-monochromated Mo Kα radiation. The crystal structures were solved by direct methods and refined by full-matrix least-squares using SHELXL-97.[16] All hydrogen atoms were placed in their ideal positions, and all non-hydrogen atoms were refined anisotropically.

General Procedure for Perfluoroalkylation. In a Pyrex glass tube were placed anthracene (0.178 g, 1.00 mmol), perfluorohexyl iodide (0.32 mL, 1.50 mmol), and CH_2Cl_2 (25.0 mL). Then $Na_2S_2O_3$ (0.791 g, 5.00 mmol) and water (5.0 mL) were added to the mixture. After the tube was sealed, the mixture was mixed by shaking and then irradiated with a Hg lamp at room temperature for 6 h. After the reaction was completed, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (silica; hexane/EtOAc 99/1) to give the product (70%, 0.696 g).

*[trans(trans)]-10,10′-Bis(trifluoromethyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (trans,trans-**2a**).* The same procedure was employed with CF_3I instead of $C_6F_{13}I$. White solids; mp 295 °C. ^{1}H NMR (400 MHz, $CDCl_3$, at 296 K): δ 7.58 (4H, d, *J* = 8.0 Hz), 7.29−7.22 (6H, m), 7.06−6.98 (6H, m), 5.57 (2H, s), 4.86 (2H, q, *J* = 10.4 Hz). ^{13}C NMR (100 Hz, at 296 K): 130.5, 130.3, 128.8, 126.3, 51.7 (q, *J* = 27.7 Hz), 38.6. ^{19}F NMR (471 MHz, $CDCl_3$, at 296 K): δ −69.1 (6F, s, $2CF_3$). IR (KBr, cm^{-1}): 3444, 3067, 3033, 2926, 2335, 1454, 1247, 1161, 1108, 907, 697. ^{1}H NMR (500 MHz, $CDCl_3$, at 233 K): δ 7.63 (2H, d, *J* = 7.0 Hz), 7.54 (2H, d, *J* = 7.0 Hz), 7.46−7.38 (6H, m), 7.21 (2H, t, *J* = 7.5 Hz), 6.82 (2H, t, *J* = 7.5 Hz), 6.35 (2H, d, *J* = 8.0 Hz), 5.57 (2H, s), 4.92 (2H, q, *J* = 10.5 Hz). ^{13}C NMR (126 Hz, at 233 K): δ 139.9, 136.2, 130.5, 130.2, 130.0, 129.4, 128.8, 126.8, 126.5, 126.0, 125.1, 51.2 (q, *J* = 27.7 Hz), 38.1. ^{19}F NMR (471 MHz, $CDCl_3$, at 233 K): δ −68.9 (6F, s, $2CF_3$).

*[cis(trans)]-10,10′-Bis(trifluoromethyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (cis,trans-**2a**).* White solids; mp 306 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (2H, d, *J* = 7.6 Hz (*trans*)), 7.52 (2H, d, J = 7.6 Hz (*cis*)), 7.29−7.22 (4H, m), 7.00−6.96 (4H, m), 6.43 (2H, d, *J* = 6.8 Hz (*trans*)), 6.20 (2H, d, *J* = 8.0 Hz (*cis*)), 5.19 (1H, q, *J* = 9.2 Hz (*trans*)), 4.85 (1H, q, *J* = 10.4 Hz (*cis*)), 4.15 (2H, dd, *J* = 11.6, 14.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.3, 138.0, 132.9, 131.0, 130.7, 130.6, 129.1, 126.9, 126.8, 126.7, 126.4, 124.6, 56.7, 49.5 (q, *J* = 27.5 Hz), 47.1 (q, *J* = 27.5 Hz), 46.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −66.9 (6F, s, $2CF_3$). IR (KBr, cm^{-1}): 3436, 3066, 3033, 2908, 2358, 1960, 1625, 1607, 1482, 1281, 907, 667.

*[cis(cis)]-10,10′-Bis(trifluoromethyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (cis,cis-**2a**).* White solids; mp 333 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (4H, d, *J* = 7.2 Hz), 7.29−7.25 (4H, m), 6.98 (4H, t, *J* = 7.2 Hz), 6.20 (4H, d, *J* = 7.6 Hz), 4.86 (2H, q, *J* = 10.4 Hz), 4.15 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 131.9, 130.5, 129.5, 126.7, 126.6, 53.2, 49.8 (q, *J* = 26.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ −66.4 (6F, s, $2CF_3$). IR (KBr, cm^{-1}): 3443, 3066, 3031, 2363, 1951, 1607, 1485, 1325, 1294, 905, 760. HRMS (FD-TOF) *m*/*z*: [M^{2+}] calcd for $C_{20}H_{10}F_{13}$ 497.0575, found 497.0567 (mixture of *trans,trans*-**2a**, *cis,trans*-**2a**, and *cis,cis*-**2a**).

*[trans(trans)]-10,10′-Bis(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (trans,trans-**2b**).* Yellow solids; mp 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.55 (2H, m), 7.52−7.44 (4H, m), 7.37−7.31 (4H, m), 7.15 (2H, t, *J* = 7.2 Hz), 6.75 (2H, t, *J* = 7.2 Hz), 6.24 (2H, d, *J* = 7.6 Hz), 5.61(2H, s), 5.03 (2H, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 137.7, 130.9, 130.6, 130.5, 129.8, 128.7, 126.7, 126.3, 125.9, 125.6, 50.3 (t, *J* = 21.9 Hz), 39.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.7 (6F, s, $2CF_3$), −110.2 (4F, dd, J = 254.3, 531.5 Hz, $2CF_2$), −118.37 (4F, s, $2CF_2$), −121.45 (4F, s, $2CF_2$), −122.65 (4F, s, $2CF_2$), −125.99 (4F, s, $2CF_2$). IR (KBr, cm^{-1}): 3075, 3039, 2934, 2364, 1960, 1927, 1483, 1278, 1061, 806, 734, 670.

*[cis(trans)]-10,10′-Bis(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (cis,trans-**2b**).* White solids; mp 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (2H, d, *J* = 7.6 Hz (*trans*)), 7.45 (2H, d, J = 7.6 Hz (*cis*)), 7.24−7.19 (4H, m), 7.01−6.97 (4H, m), 6.50 (2H, d, *J* = 7.6 Hz (*trans*)), 6.24 (2H, d, *J* = 8.0 Hz (*cis*)), 5.40 (1H, t, *J* = 16.8 Hz (*trans*)), 5.11 (1H, t, *J* = 15.6 Hz (*cis*)), 4.24 (2H, dd, *J* = 11.6, 24.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.4, 138.7, 133.8, 131.2, 130.7, 130.6, 128.7, 127.1, 126.6, 126.4, 126.3, 125.2, 56.5, 48.4 (t, *J* = 23.9 Hz), 46.9, 46.0 (t, *J* = 21.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.6 (6F, s, $2CF_3$), −105.1 (2F, s, CF_2), −115.5 (2F, s, CF_2), −118.8 (2F, s, CF_2), −121.3 (4F, s, $2CF_2$), −122.2 (2F, s, CF_2), −122.6 (4F, s, $2CF_2$), −125.9 (4F, s, $2CF_2$). IR (KBr, cm^{-1}): 3434, 3073, 3036, 2930, 2362, 1481, 1457, 1202, 949, 695.

*[cis(cis)]-10,10′-Bis(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)-9,9′,10,10′-tetrahydro-9,9′-bianthracene (cis,cis-**2b**).* White solids;

mp 261 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (4H, d, J = 8.0 Hz), 7.28−7.24 (4H, m), 7.15 (4H, t, J = 7.6 Hz), 6.30 (4H, d, J = 7.2 Hz), 5.14 (2H, t, J = 16.0 Hz), 4.18 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 132.1, 130.5, 130.2, 126.8, 126.6, 53.0, 48.6 (t, J = 23.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.6 (6F, s, $2CF_3$), −105.1 (4F, s, $2CF_2$), −119.2 (4F, s, $2CF_2$), −121.2 (4F, s, $2CF_2$), −122.6 (4F, s, $2CF_2$), −125.9 (4F, s, $2CF_2$). IR (KBr, cm^{-1}): 3444, 3028, 2925, 2908, 2849, 2361, 1627, 1456, 1245, 1143, 1063, 735, 695. Anal. Calcd for $C_{40}H_{20}F_{26}$: C, 48.31; H, 2.03. Found: C, 48.12; H, 2.07 (mixture of *trans,trans*-**2b**, *cis,trans*-**2b**, and *cis,cis*-**2b**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01655.

X-ray data for *cis,cis*-**2a** (CIF)

X-ray data for *cis,trans*-**2a** (CIF)

X-ray data for *trans,trans*-**2a** (CIF)

Experimental procedures, physical properties, and calculation data (PDF)

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Notes

The authors declare no competing financial interest.

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