Thermal and Photochemical Isomerization of Tetraaryl Tetrakis(trifluoromethyl)[4]radialenes

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The isomerization of tetraaryl tetrakis(trifluoromethyl)[4]radialenes was studied. When type II (all-Z) isomers of 5,6,7,8-tetraaryl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialenes were heated in tetralin at 170−200 °C, isomerization occurred to give mixtures of four [4]radialenes in a ratio of ca. I:II:III:IV = 1:10:5:1. However, when the isomeric mixtures were heated in the solid state at the same temperature, selective isomerization took place to give type II isomers in good selectivity (>91%). Upon irradiation with light, the type II isomers first isomerized to mixtures of the four [4]radialene isomers (I:II:III:IV = 2:2:48:48) and then rearranged to cyclobuta[*b*]naphthalenes via a 6π-electrocyclic reaction followed by 1,3-hydrogen migration.

Introduction

The cross-conjugated π-electron system of radialenes is reported to show interesting properties such as ferromagnetism and multiredox potential.[1] Although many synthetic methods for accessing these compounds have been reported so far, most of the successful examples are limited to the preparation of highly symmetric radialenes,[1,2] where the isomerization and determination of radialene isomers need not be considered. Even fundamental reactions of radialenes such as isomerization have been hardly investigated, probably because of the difficulty of monitoring the progress of the reaction and of determining the structure of the isomers. Generally, the ^{19}F NMR technique is useful for monitoring the course of reactions, if the molecules have a few fluorine atoms, because of the wide chemical shifts, high nuclear sensitivity, and transparency toward not only other parts of molecules but also solvents. Moreover, the spatial proximity between fluorine atoms and other NMR-sensitive nuclei can be easily determined by through-space coupling[3] without using the NOE technique. We previously succeeded in determining four isomers of 5,6,7,8-tetraaryl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialenes using ^{19}F NMR and revealed selective isomerization to the type II (all-Z) isomer in the solid state.[4] In this study, we examined isomerization of [4]radialenes involving photochemical rearrangement. For brevity, we used I, II, III, and IV as the types of the four isomers analogously to the porphyrin chemistry instead of 1*E*,2*E*,3*E*,4*E*, 1*Z*,2*Z*,3*Z*,4*Z*, 1*Z*,2*Z*,3*E*,4*E*, and 1*Z*,2*E*,3*Z*,4*E* (Figure 1).[5]

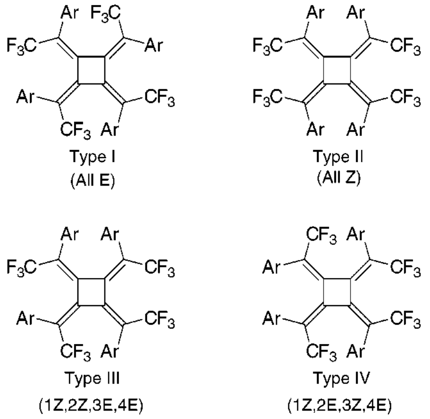

Figure 1. Four isomers of tertraayl tetrakis(trifluoromethyl)-[4]radialenes.

Results and Discussion

Preparation of Tetraaryl Tetrakis(trifluoromethyl)-[4]radialenes. 5,6,7,8-Tetraaryl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialenes (**3**) were prepared by the coupling reaction[6] of the corresponding dibromostyrenes **1** or the thermal dimerization of cumulenes **2** (Scheme 1).[7] The coupling reaction of **1** with Zn−CuBr was carried out below −60 °C to give isomeric [4]radialenes **3** in addition to cumulenes **2**.[8] The four isomers could be separated only in the case of **3a** by a combination of repeated silica gel chromatography, preparative GPC, and fractional recrystallization. In other cases, complete separation of the isomers was not achieved partially as a result of the instability of these radialenes, although isomeric mixtures of radialenes could be separated from other byproducts. The homogeneity of these [4]radialenes was unambiguously proven by thermal reversible isomerization (vide post). During isolation, new signals appeared in ^{19}F

[†] Department of Chemistry, Faculty of Science.

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10.1021/jo990699v CCC: $19.00

Scheme 1

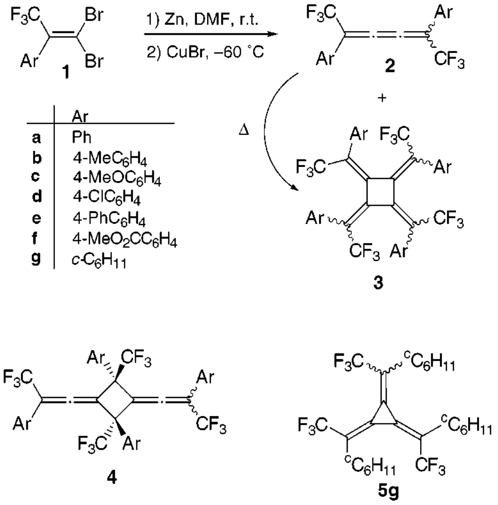

Table 1. Thermal Dimerization of Cumulenes 2

run	substrate	temp °C	time h	yield %[a]	ratio[a] I:II:III:IV
1	**2a**	150	24	90	3:58:29:10
2	**2a**	200	2	80	5:45:42:8
3	**2b**	150	24	90	6:68:19:7
4	**2b**	200	2	90	3:58:29:10
5	**2c**	150	24	85	2:64:31:3
6	**2c**[b]	200	2	40[c]	4:62:28:6
7	**2d**	150	24	70	3:64:24:9
8	**2d**	200	2	60	2:71:22:5
9	**2e**	150	24	0	
10	**2e**[d]	170	48	90[c]	6:54:24:14
11	**2e**[d]	200	4	80[c]	3:61:29:7
12	**2e**	200	4	80	1:95:3:1
13	**2f**	150	24	0	
14	**2f**	170	48	40	type II >90[e]
15	**2f**	200	2	45	3:61:29:7

[a] The yield and ratio were roughly calculated from ^{19}F NMR spectra of the reaction mixture. [b] The purity was 70%. [c] The yield was based on the purity of cumulene. [d] The purity was 56%. [e] The isomeric ratio could not be estimated.

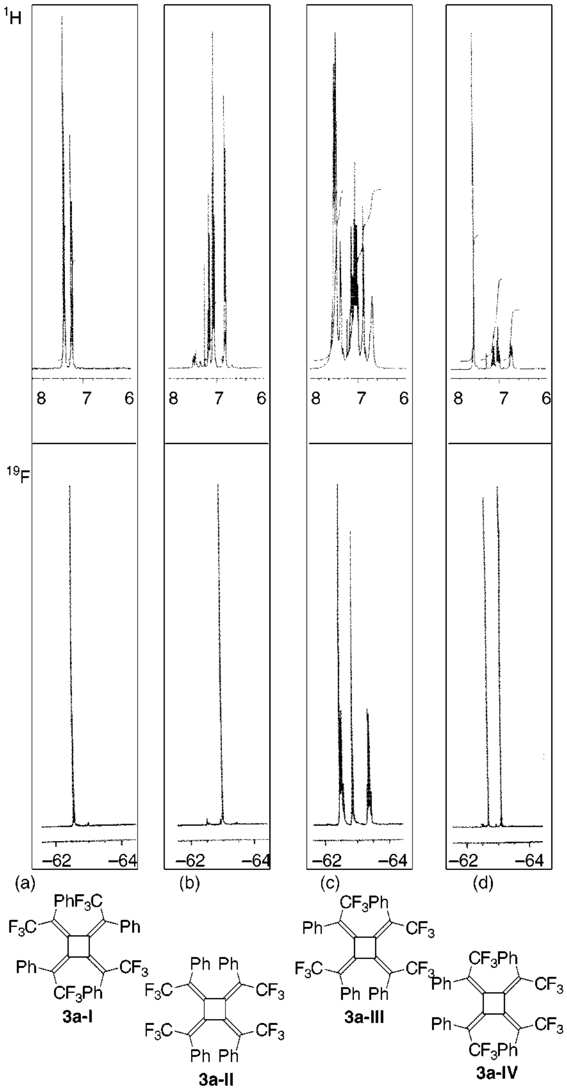

Figure 2. Four isomers of [4]radialenes: (a) **3a-I**; (b) **3a-II**; (c) **3a-III**; (d) **3a-IV**.

NMR spectra in some cases. One of the newly formed compounds in the reaction of **1d** could be isolated and its structure was determined to be *trans-anti*-1,3-bis(vinylidene)cyclobutane **4d** by X-ray analysis (see Supporting Information). This 1,3-bis(vinylidene)cyclobutane **4** would be derived from cumulenes, since the formation of this skeleton has been reported in the photodimerization of tetraaryl cumulenes in the solid state.[9] The coupling reaction of cyclohexyl derivative **1g** afforded a complex mixture, from which [3]radialenes **5g**, in addition to [3]cumulenes **2g** and [4]radialenes **3g**, were obtained in an impure form by repeated column chromatography and GPC. The cumulenes **2** were also converted to the [4]radialenes **3** by heating neat at 150−200 °C for 2−48 h (Table 1). The isomeric ratios and yields were determined by ^{19}F NMR analysis of the reaction mixtures. In all cases except for runs 12 and 14, all of the isomers of [4]radialenes **3** were formed, as well as unidentified products. In runs 12 and 14, type II isomers were predominantly formed. In these cases, the starting materials **2e** and **2f** did not melt,[10] whereas in other cases the starting cumulenes melted gradually or immediately. Pure type II isomers of [4]radialenes **3** were easily obtained in 15−40% yields by recrystallization of the chromatographed mixtures.

Structure Determination of [4]Radialene Isomers. The stereochemistry of [4]radialene isomers **3a** was unambiguously determined by ^{19}F and ^{1}H NMR (Figure 2). Type III and IV isomers were easily identified because of their low symmetricity. Two singlets and a pair of quartets (ca. $J = 10$ Hz) with the same intensity were observed in the type III isomers and two singlets were seen in the type IV isomers. On the other hand, the type I and II isomers could not be distinguished by ^{19}F NMR. Fortunately, the type I and II isomers (**3a-I** and **3a-II**) were assigned by ^{1}H NMR analysis on the basis of an upfield shift of the aromatic protons of the type II isomer **3a-II** due to the anisotropic effect of the stacking aromatic rings. All of the protons of four phenyl groups in **3a-II** and the protons of two phenyl groups in **3a-III** and **3a-IV** appeared at higher fields than chloroform, whereas all of the aromatic protons of **3a-I** were at lower fields. This assignment was confirmed by X-ray

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(10) In the solid state, the type II [4]radialene was reported to be predominantly formed in the thermal dimerization of dimethyl 2,5-diphenylhexa-2,3,4-trienedioate; see ref 5.

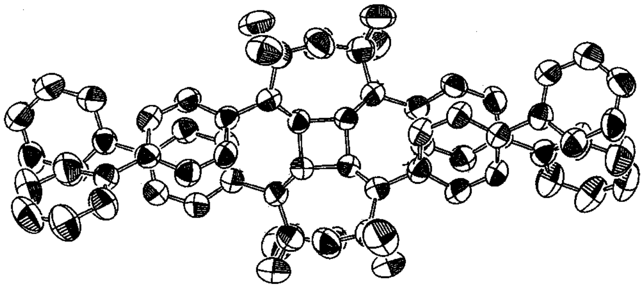

Figure 3. Ortep drawing of **3e-II**.

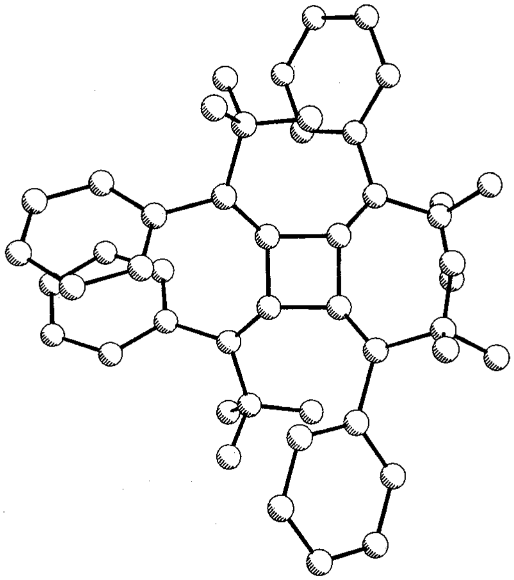

Figure 4. Pluto representation of **3e-IV**.

Table 2. Thermal Isomerization of [4]Radialenes 3

run	sub-strate	starting I:II:III:IV	conditions			final I:II:III:IV
			solvent	temp °C	time	
1	**3a**	0:97:3:0	tetralin[a]	170	5 min	3:70:24:3
					30 min	6:57:32:5
					20 h	7:56:32:5
2	**3a**	7:56:32:5	neat	170	24 h	2:87:9:2
3	**3a**	79:2:14:5	neat	150	24 h	2:95:3:tr
4	**3a**	0:0:0:>99	neat	150	2 h	1:64:2:33
					70 h	1:97:1:1
5	**3a**	2:2:85:11	neat	150	24 h	2:2:85:11
6	**3a**	2:2:85:11	neat	200	2 h	2:83:12:3
7	**3b**	0:>99:0:0	tetralin[a]	170	23 h	5:61:28:6
8	**3b**	5:61:28:6	neat	170	6 h	1:96:2:1
9	**3c**	0:98:2:0	$C_6D_5CD_3$[a]	100	112 h	4:70:22:4
10	**3c**	4:56:33:7	neat	150	24 h	1:96:2:1
11	**3c**	4:56:33:7	neat	170	24 h	1:93:5:1
12	**3c**	4:56:33:7	neat	200	2 h	5:77:9:9
13	**3d**	1:67:23:9	neat	170	24 h	7:91:1:1
14	**3e**	0:>99:0:0	tetralin[a]	200	3 h	3:63:26:8
15	**3e**	3:63:26:8	neat	200	4 h	tr:97:3:tr
16	**3f**	0:>99:0:0	tetralin[a]	170	17.5 h	5:59:29:7[b]
17	**3f**	5:59:29:7[b]	neat	170	9 h	tr:97:3:tr[c]
18	**3g**	6[d]:1[d]:75:18	neat	200	2 h	6[d]:1[d]:75:18
19	**3g**	6[d]:1[d]:75:18	neat	240	13.5 h	*e*
20	**3g**	0[d]:>99[d]:0:0	tetralin[a]	200	2 h	tr[d]:88[d]:12:tr
					142 h	10[d]:47[d]:36:7[f]

[a] The concentration was ca. 10%. [b] The purity of [4]radialenes was ca. 90%. [c] The purity of [4]radialenes was ca. 72%. [d] The assignment of **3g-I** and **3g-II** could not be done. [e] Considerable decomposition was observed, and the ratio could not be estimated. [f] The purity of [4]radialenes was ca. 63%.

analyses of **3e-II** and **3a-IV** (Figures 3 and 4). In these figures, trifluoromethyl groups are quite close to each other, and the distances between their center carbons are 3.71 Å in **3a-IV** and 3.70 and 3.75 Å in **3e-II**. These trifluoromethyl groups are, of course, equivalent and do not have coupling constants. Although X-ray analysis of the type III isomer **3a-III** was not done, a similar proximity between the trifluoromethyl groups would be expected, and this could explain the large through-space coupling constant (10 Hz). On the basis of this structure determination of **3a**, the structures of the other radialene isomers **3b**−**f** were assigned by comparison of their ^{19}F NMR spectra.

Thermal Isomerization of [4]Radialenes. In the preparation of [4]radialenes, different isomeric ratios were observed as the conditions varied. The thermal isomerization of [4]radialenes was examined in solution or in the solid state, and the results are summarized in Table 2. A ca. 10% solution of **3a-II** (I:II:III:IV = 0:97:3:0) in tetralin was heated at 170 °C in an NMR tube, and the progress was monitored by ^{19}F NMR. The ratio reached 6:57:32:5 in 30 min and did not change thereafter. This ratio is almost the same as that obtained in the thermal dimerization of **2a** (Table 1, run 1). When this isomeric mixture was heated at the same temperature in the solid state after removal of the solvent, the ratio was 2:87:9:2 after 24 h. During both isomerizations, no byproduct was detected by ^{19}F NMR. The predominant formation of **3-II** was also realized in the thermal isomerization of other tetraaryl [4]radialenes in the solid state (Table 2). The thermal stability of [4]radialenes is quite good, and no formation of byproducts at these temperatures was observed, except for **3f** at 170 °C and **3g** at 240 °C. In the case of the *c*-hexyl derivative **3g**, however, isomerization in the solid state was slow even at 200 °C, and no distinct preference for the formation of any isomer was observed at 240 °C.

One reason the type II isomers are preferentially formed both in solution and in the solid state is the effect of stacking,[11] which could overwhelm the unfavorable steric interaction of large trifluoromethyl groups.[12] This is supported by the fact that no preference for the formation of any isomer was seen in the *c*-hexyl derivative **3g** (runs 18−20). Let us consider the mechanism of this isomerization. Cycloreversion of radialenes to cumulenes followed by recombination does not seem to be applicable in this case; no formation of cumulenes was observed and no crossover radialene was detected when radialenes **3a** and **3c** were heated at 170 °C in tetralin. Thus, rotation of the exomethylene double bonds must occur during isomerization. If only one exomethylene double bond rotates, type I and IV isomers must isomerize first to type III and then to type II. However, the type I and IV isomers of **3a** easily isomerized to **3a-II** at 150 °C for 24 h, whereas the sample containing **3a-III** as the major component did not isomerize under the same conditions (runs 3−6). Although some diradical processes that have been proposed for the thermal [4 + 4] dimerization of the parent radialene[13] might be applicable in this isomerization, the reason is not clear.

Photochemical Isomerization of [4]Radialenes. In preparating single crystals for X-ray analysis, the slow

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(11) For recent examples for aromatic π−π interaction, see: Ranganathan, D.; Haridas, V.; Gilardi, R.; Karle, L. I. *J. Am. Chem. Soc.* **1998**, *120*, 10793. Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019.

(12) Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5618.

(13) Hopf, H.; Trabert, L. *Liebigs Ann. Chem.* **1980**, 1786.

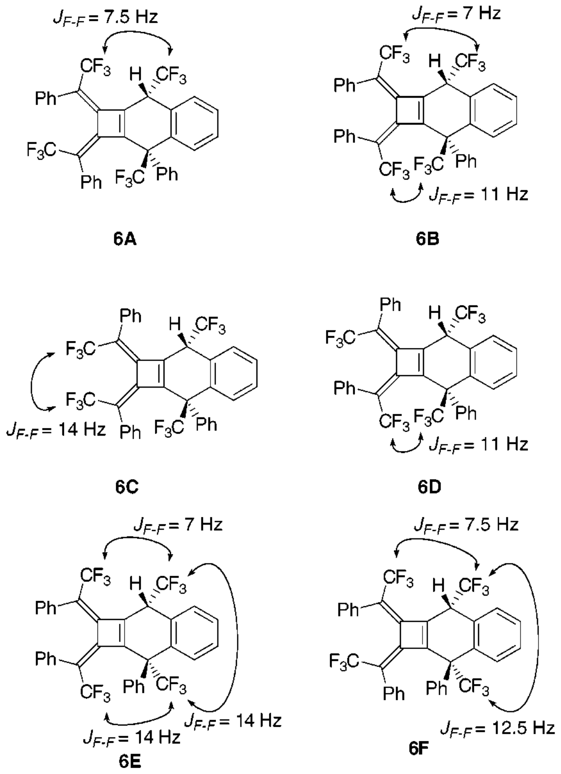


Figure 5. Assigned structures of cyclobuta[*b*]naphthalenes **6**. Structures **6B** and **6D** are tentative assignments based on only ^{19}F NMR spectra.

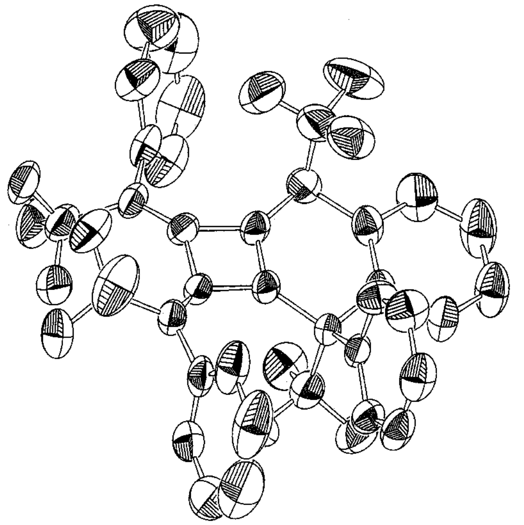


Figure 6. Ortep drawing of **6C**.

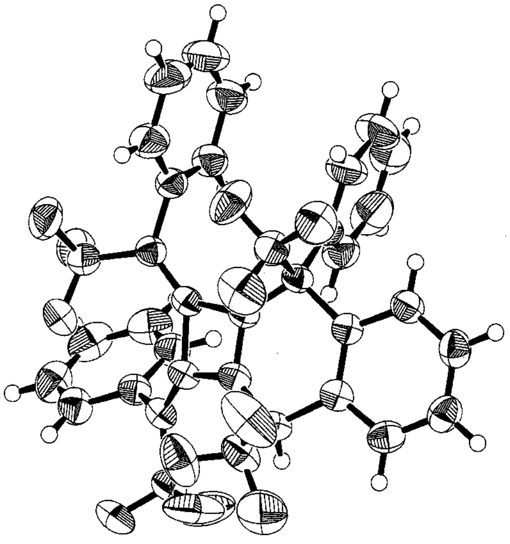


Figure 7. Ortep drawing of **6F**.

solvent-evaporation method was used for [4]radialene isomers. The type II isomer **3a-II** was dissolved in toluene (ca. 0.1 g/mL) and left in a laboratory. Even after 22 days, no crystallization was observed. From the ^{19}F NMR spectra of this sample, **3a-II** isomerized into a mixture of [4]radialene isomers (I:II:III:IV = 1:28:47:24), as well as two new compounds **6A** and **6B** (A:B = 36:64). After 130 d, all four [4]radialenes disappeared and at least nine other compounds were detected. Four major isomers **6A**, **6C**, **6E**, and **6F** were isolated by chromatography on silica gel and preparative GPC followed by repeated fractional recrystallization. These compounds showed distinctive features in ^{1}H and ^{19}F NMR spectra. An aliphatic methine proton was observed at δ 5.05 (7.3 Hz), 3.85 (7.6 Hz), 5.17 (7.5 Hz), and 5.11 (7.8 Hz) as a quartet in the respective ^{1}H NMR spectra of **6A**, **6C**, **6E**, and **6F**. This indicated that the methine groups were adjacent to a CF_3 group. By NMR analyses, these compounds were revealed to have a cyclobuta[*b*]naphthalene skeleton. On the basis of the long-range coupling constants of F−F, the stereochemical structures were determined as illustrated in Figure 5. These assignments are supported by the unambiguous structure determination of **6C** and **6F** by X-ray analysis (Figures 6 and 7). Other products in the mixture could not be isolated, and their structures were not determined, although the two other major products were supposed to have structures **6B** and **6D** illustrated in Figure 5, based on ^{19}F NMR.

This reaction must be driven by light irradiation. Photochemical investigations of [4]radialenes are very rare.[1] Thus, the photochemical behavior of the [4]radialenes was examined, and the results are summarized in Table 3. The cyclobuta[*b*]naphthalenes **6A**−**F** were all shown to be photostable (run 6). In the isomerization of **3a-II**, **6B** was preferentially formed first and the two other major isomers **6A** and **6C** were then formed, after isomerization between the [4]radialenes was complete (runs 1 and 2).

The type II isomers of [4]radialenes **3** show distinctive fluorescence on TLC and in the solid state compared to other isomers. UV and fluorescence spectra of all of the isomers **3a** were measured in *n*-hexane (Table 4). As shown in this Table, the absorption maxima of the four isomers are almost the same, and the absorption coefficients increase as the symmetricity decreases. The fluorescence quantum yields increase in the order type IV < I < III < II. The higher yield of **3a-III** compared to **3a-IV** and **3a-I** may be due to the restricted movement of exomethylene moieties observed in ^{1}H NMR. The unexpectedly small difference in quantum yields between **3a-II** and other isomers may be related to the easy photoisomerization of **3a-II** to other isomers *in solution*. In fact, no isomerization of **3a-II** was observed *in the solid state* after 35 h of irradiation with light.

The formation of cyclobuta[*b*]naphthalene isomers **6A**−**F** can be adequately explained by the Woodward−Hoffmann rule. The possible isomerization routes starting from the type II isomer **3a-II** is illustrated in Scheme 2. First, the antarafacial 6π-electrocyclic reaction would

Table 3. Photochemical Isomerization of [4]Radialenes 3

		conditions		ratio[a]			
				radialenes **3**		cyclobuta[*b*]naphthalenes **6**	
run	substrate	$h\nu$[b]	time	%	I:II:III:IV	%	A:B:C:D:E:F[c]
1	**3a-II**	A	22 d	78	1:28:47:24	22	36:64:—[d]:—[d]:—[d]:—[d]
			67 d	32	—[d]:9:41:50	64	31:30:15:3:7:6
			130 d	0	—	90	44:27:17:2:6:4
2	**3a-II**	B	30 min	87	4:18:44:34	12	33:29:11:4:18:5
			1 h	73	6:9:41:44	25	29:24:14:3:18:12
			2 h	59	4:8:44:44	31	32:13:16:—[d]:23:16
			10 h	7	—[d]:10:39:51	35	30:16:11:—[d]:20:23
3	**3a-I**	A	90 d	24	8:17:46:29	38	39:16:21:5:13:5
4	**3a-IV**	A	180 d	3	*e*	84	43:6:38:2:5:6
5	**3a**[f]	B	1 h	0		94	41:11:19:4:18:7
			2 h	0		81	43:10:21:4:16:6
6	**6**[g]	A	42 d			100	45:28:13:3:7:4

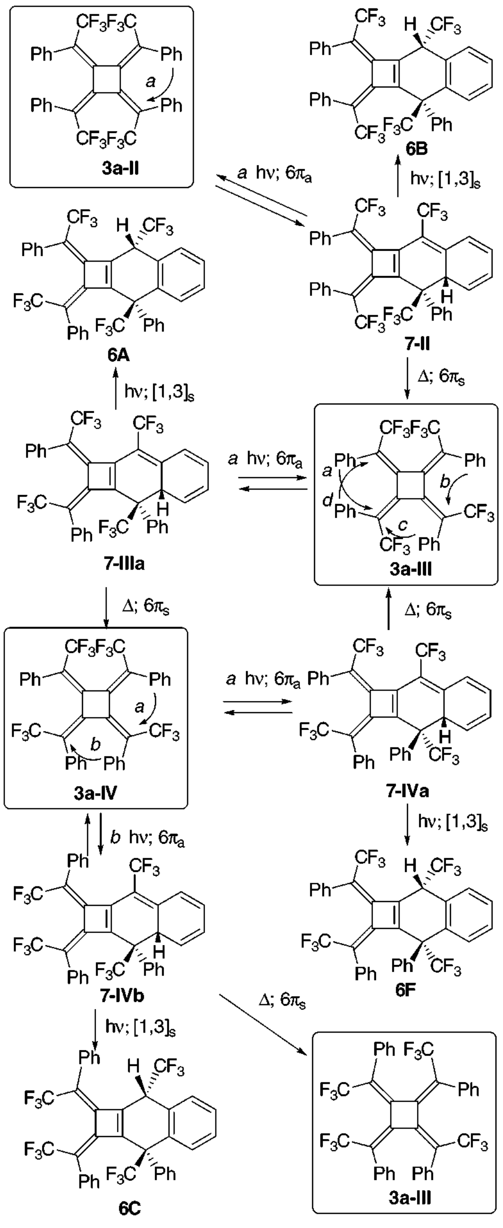
[a] The ratio was calculated on the basis of an analysis of the ^{19}F NMR spectra. [b] A: The substrate was dissolved in toluene (ca. 0.1 g/mL) and left in a room without protection from light. B: The substrate was dissolved in benzene (0.005 mol/L) and irradiated by a 40-W UV lamp. [c] Structures B and D are tentative. [d] The ratio could not be determined because of signal overlapping. [e] Only type IV **3a-IV** could be detected. [f] A mixture of isomers (I:II:III:IV = 4:25:52:19) containing **6E** (17%) was used. [g] A mixture of **6** (A:B:C:D:E:F = 45:28:13:3:7:4) was used.

Table 4. Fluorescence Quantum Yields and Absorption Coefficients of 3a

	UV		fluorescence	
compound	λ_{max} nm	$\epsilon \times 10^5$ $M^{-1}\,cm^{-1}$	λ_{max} nm	Φ_f[a] $\times 10^{-3}$
3a-I	334	1.26	450	2.4
3a-II	337	1.66	460	4.1
3a-III	348	2.24	464	2.9
3a-IV	334	1.74	471	1.6

[a] The quantum yield was calculated by using a 0.5 N solution of quinine sulfate as a standard (Φ_f = 0.546).

Scheme 2. Photoisomerization of 3a-II



give the intermediate **7-II**, and this reaction should be photoreversible. Thus, there would be three possible fates for this intermediate **7-II**: going back to **3a-II**, leading to the cyclobuta[*b*]naphthalene **6B** via 1,3-hydrogen shift by absorbing another photon, and giving the type III radialene **3a-III** through a thermal 6π-electrocyclic ring opening process. The type III radialene **3a-III** would be, in turn, photoisomerized through four inermediates **7-III**, one of which leading to **6A** and **3a-IV** is illustrated in Scheme 2. The isomerization of **3a-IV** would give only the type III radialene **3a-III** and two cyclobuta[*b*]naphthalenes **6C** and **6F**. The other cyclobuta[*b*]naphthalenes **6D** and **6E** would be formed from **3a-III**.

Because an intermediate such as **7** was not detected in any experiment and the photon density was low (room light), the thermal process resulting in the isomerization between the radialenes would be the main pathway. In fact, the isomerization between the radialene isomers reached an equilibrium within 30 min under the irradiation of a 40 W fluorescent lamp (Table 3, run 2). As the absorption maxima of the radialene isomers are ca. 340 nm, the intermediates **7** are expected to absorb visible light as a result of low symmetry. Therefore, there would be a fair chance for **7** to absorb anothor photon, causing a 1,3-hydrogen shift.

Conclusion

In the solid state, 5,6,7,8-tetraaryl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialenes isomerized to type II isomers in more than 90% selectivity at appropriate temperatures (>150 °C), whereas in solution, equilibrium mixtures of ca. I:II:III:IV = 1:10:5:1 were obtained. On the other hand, upon irradiation with light, the type II isomers easily first isomerized to ca. 1:1:5:5 mixtures of [4]radialene isomers and then underwent a $6\pi_a$-electrocyclic reaction followed by a 1,3-hydrogen shift to afford cyclobuta[*b*]naphthalenes.

Experimental Section

Dimerization of Cumulenes 2. Typical Procedure (Table 1, run 1). The cumulene **2a** (340 mg, 1 mmol) was placed in a flask, and then the flask was purged with argon. The flask was put in a preheated glass-tube oven at 150 °C. After 24 h, the gummy solid was subject to NMR analysis and then chromatographed on silica gel (3−5% EtOAc/hexane) to give 251 mg (74%) of radialene isomers **3a** (I:II:III:IV = 1:20:10:3), as well as the recovered **2a** (19 mg, 6%). Purity of the radialene isomers was ca. 90% estimated by ^{19}F NMR. Separation of the isomers was carried out by the combination of preparative GPC and fractional recrystallization from CH_2Cl_2/hexane.

Thermal Isomerization of Radialenes (3) in Tetralin. Typical Procedure (Table 2, run 1). The radialene **3a-II** (40 mg) was dissolved in tetralin (0.4 mL), and the solution was introduced in a 5-mm NMR tube. After the solution was bubbled with argon for 15 min, an inner tube containing DMSO-d_6 was inserted, and the tube was capped. The sample tube was placed in a NMR probe and then heated to 170 °C. The ^{19}F NMR spectra were taken after the indicated time in Table 2.

Thermal Isomerization of Radialenes (3) in Solid. Typical Procedure (Table 2, run 4). Isomerization of **3a-IV** (40 mg) was performed similarly as the dimerization described above. After 2 h, 4 mg of the sample was taken out for ^{19}F NMR analysis. After 70 h, the remaining solid was subject to the NMR analysis and then recrystallized from hexane (1 mL) to give 25 mg (63%) of pure type II isomer **3a-II**.

5,6,7,8-Tetraphenyl-5,6,7,8-tetrakis(trifluoromethyl)-[4]radialene (3a). MS *m*/*z* 680 (M^+), 611, and 340. Anal. Calcd for $C_{36}H_{20}F_{12}$: C, 63.54; H, 2.96. Found: C, 63.44; H, 3.14. **3a-I (type I isomer):** $R_f = 0.45$ (5% EtOAc/hexane); pale yellow crystals, mp 196−198 °C (decomp); ^{1}H NMR δ 7.28 (8H, m) and 7.38−7.48 (12H, m); ^{13}C NMR δ 122.2 (q, $J = 275$ Hz), 122.8 (q, $J = 33$ Hz), 128.1, 128.7, 129.6, 132.3, and 137.1 (br); ^{19}F NMR δ −62.56 (s); IR (KBr) 1322s, 1224vs, 1176vs, 1130vs, and 1058s cm^{-1}. **3a-II (type II isomer):** $R_f = 0.45$ (5% EtOAc/hexane); pale yellow crystals, mp 180−224 °C (decomp); ^{1}H NMR δ 6.82 (8H, m), 7.06 (8H, m), and 7.16 (4H, m); ^{13}C NMR δ 122.6 (q, $J = 275$ Hz), 122.6 (q, $J = 37$ Hz), 127.8, 128.5, 128.7, 131.7, and 137.5 (br); ^{19}F NMR δ −63.01 (s); IR (KBr) 1318s, 1222s, 1208s, 1174vs, 1128vs, and 1060s cm^{-1}. **3a-III (type III isomer):** $R_f = 0.4$ (5% EtOAc/hexane); pale yellow crystals, mp 180−181 °C (decomp); ^{1}H NMR δ 6.70 (2H, br m), 6.87 (2H, m), 6.95−7.2 (6H, m), 7.34 (2H, m), and 7.4−7.55 (8H, m); ^{13}C NMR δ 121.7 (q, $J = 275$ Hz), 122.0 (q, $J = 275$ Hz), 122.2 (q, $J = 33$ Hz), 122.6 (q, $J = 274$ Hz), 122.6 (q, $J = 33$ Hz), 122.9 (q, $J = 274$ Hz), 123.2 (q, $J = 33$ Hz), 124.5 (q, $J = 34$ Hz), 127.7, 127.8, 128.1, 128.4, 128.4, 128.5, 128.6, 128.6, 128.8, 128.8, 129.5, 129.6, 131.7, 131.8, 132.5, 132.7, 136.8 (br), 137.6 (br, 2 carbons), and 137.9 (br); ^{19}F NMR δ −63.40 (3F, q, $J = 10$ Hz), −62.89 (3F, s), −62.54 (3F, q, $J = 10$ Hz), and −62.48 (3F, s); IR (KBr) 1322vs, 1222s, 1208s, 1174vs, 1126vs, and 1060s cm^{-1}. **3a-IV (type IV isomer):** $R_f = 0.35$ (5% EtOAc/hexane); pale yellow crystals, mp 194−196 °C (decomp); ^{1}H NMR δ 6.72 (4H, m), 6.99 (4H, m), 7.09 (2H, m), and 7.49 (10H, m); ^{13}C NMR δ 121.6 (q, $J = 275$ Hz), 122.3 (q, $J = 33$ Hz), 122.8 (q, $J = 276$ Hz, CF_3), 124.6 (q, $J = 34$ Hz), 127.7, 128.4, 128.5, 128.7, 128.7, 129.6, 131.9, 132.7, 137.2 (br), and 137.9 (br); ^{19}F NMR δ −62.68 (6F, s) and −63.09 (6F, s); IR (KBr) 1320vs, 1222s, 1208s, 1174vs, 1128vs, and 1058s cm^{-1}.

5,6,7,8-Tetra-*p*-tolyl-5,6,7,8-tetrakis(trifluoromethyl)-[4]radialene (3b). MS *m*/*z* 736 (M^+), 667, and 368. Anal. Calcd for $C_{40}H_{28}F_{12}$: C, 65.22; H, 3.83. Found: C, 65.40; H, 4.12. **3b-I (type I isomer):** ^{19}F NMR δ −62.44 (s). **3b-II (type II isomer):** pale yellow crystals, mp 220−221 °C (decomp); ^{1}H NMR δ 2.28 (12H, s), 6.72 (8H, m), and 6.84 (8H, m); ^{13}C NMR δ 21.2 (Me), 122.1 (m), 122.7 (q, $J = 275$ Hz), 127.9, 128.8, 128.9, 137.5 (br), and 138.6; ^{19}F NMR δ −62.87 (s); IR (KBr) 1322s, 1224s, 1172vs, 1164vs, 1130vs, and 1070s cm^{-1}. **3b-III (type III isomer):** ^{19}F NMR δ −62.34 (3F, s), −62.51 (3F, q, $J = 10$ Hz), −62.85 (3F, s), and −63.27 (3F, q, $J = 10$ Hz). **3b-IV (type IV isomer):** ^{19}F NMR δ −62.49 (6F, s) and −63.10 (6F, s).

5,6,7,8-Tetra-*p*-methoxyphenyl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialene (3c). MS *m*/*z* 800 (M^+), 739, and 400. Anal. Calcd for $C_{40}H_{28}F_{12}O_4$: C, 60.01; H, 3.52. Found: C, 60.07; H, 3.67. **3c-I (type I isomer):** ^{19}F NMR δ −62.22 (s). **3c-II (type II isomer):** yellow crystals, mp 195−210 °C (decomp); ^{1}H NMR δ 3.78 (12H, s), 6.59 (8H, m), and 6.81 (8H, m); ^{13}C NMR δ 55.2 (Me), 113.7, 121.4 (m), 121.5 (q, $J = 276$ Hz), 124.2, 129.4, 137.4 (br), and 160.0; ^{19}F NMR δ −62.61 (s); IR (KBr) 1320s, 1292s, 1256s, 1224s, 1170vs, and 1128vs cm^{-1}. **3c-III (type III isomer):** ^{19}F NMR δ −61.98 (3F, s), −62.39 (3F, q, $J = 10$ Hz), −62.71 (3F, s), and −63.00 (3F, q, $J = 10$ Hz). **3c-IV (type IV isomer):** ^{19}F NMR δ −62.01 (6F, s) and −63.12 (6F, s).

5,6,7,8-Tetra-*p*-chlorophenyl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialene (3d). MS *m*/*z* 820 [$M^+(^{37}Cl_2)$], 818 [$M^+(^{37}Cl^{35}Cl)$], and 816 [$M^+(^{35}Cl_2)$]. Anal. Calcd for $C_{36}H_{16}Cl_4F_{12}$: C, 52.84; H, 1.97. Found: C, 52.62; H, 1.94. **3d-I (type I isomer):** ^{19}F NMR δ −62.47 (s). **3d-II (type II isomer):** pale yellow crystals, mp 255−257 °C (decomp); ^{1}H NMR δ 6.78 (8H, m) and 7.12 (8H, m); ^{13}C NMR δ 122.1 (q, $J = 276$ Hz), 122.4 (m), 128.8, 129.3, 129.8, 135.7, and 137.3 (br); ^{19}F NMR δ −63.05 (s); IR (KBr) 1320vs, 1220s, 1172vs, 1134vs, and 1096s cm^{-1}. **3d-III (type III isomer):** ^{19}F NMR δ −62.31 (3F, s), −62.72 (3F, q, $J = 10$ Hz), −62.88 (3F, s), and −63.47 (3F, q, $J = 10$ Hz). **3d-IV (type IV isomer):** ^{19}F NMR δ −62.46 (6F, s), and −63.35 (6F, s).

1,3-Di-*p*-chlorophenyl-2,4-bis[2-(*p*-chlorophenyl)ethenylidene]-1,3-bis(trifluoromethyl)cyclobutane (4d). ***trans-anti* Isomer:** pale yellow crystals, mp 235−237 °C; ^{1}H NMR δ 7.32 (4H, m), 7.35 (4H, m), and 7.46 (8H, m); ^{19}F NMR δ −60.42 (6F, s) and −73.70 (6F, s); IR (KBr) 1978w, 1902w, 1496s, 1298s, 1166vs, 1138vs, and 1098vs cm^{-1}. Anal. Calcd for $C_{36}H_{16}Cl_4F_{12}$: C, 52.84; H, 1.97. Found: C, 52.48; H, 1.79. **Another isomer:** ^{1}H NMR δ 7.20 (8H, m) and 7.50 (8H, m); ^{19}F NMR δ −60.97 (6F, s), and −73.10 (6F, s).

5,6,7,8-Tetra-4-biphenylyl-5,6,7,8-tetrakis(trifluoromethyl)[4]radialene (3e). MS *m*/*z* 984 (M^+), 915, and 492. Anal. Calcd for $C_{60}H_{36}F_{12}$: C, 73.17; H, 3.68. Found: C, 73.09; H, 3.95. **3e-I (type I isomer):** ^{19}F NMR δ −62.22 (s). **3e-II (type II isomer):** $R_f = 0.4$ (5% EtOAc/hexane); yellow prismatic crystals (toluene), mp > 300 °C; ^{1}H NMR δ 6.98 (4H, m, $H^{2'}$ and $H^{6'}$), 7.25 (4H, m, $H^{3'}$ and $H^{5'}$), and 7.35−7.45 (10H, m, Ph); ^{13}C NMR δ 122.3 (q, $J = 38$ Hz), 122.7 (q, $J = 276$ Hz), 126.9, 127.8, 128.5, 128.9, 130.7, 137.6 (m), 140.1, and 141.6; ^{19}F NMR δ −62.54 (s). IR (KBr) 1322s, 1224s, 1174vs, and 1128vs cm^{-1}. **3e-III (type III isomer):** ^{19}F NMR δ −60.14 (3F, s), −62.28 (3F, q, $J = 10$ Hz), −62.65 (3F, s), and −62.96 (3F, q, $J = 10$ Hz). **3e-IV (type IV isomer):** ^{19}F NMR δ −62.20 (6F, s) and −62.94 (6F, s).

5,6,7,8-Tetra-*p*-methoxycarbonylpnenyl-5,6,7,8-tetrakis-(trifluoromethyl)[4]radialene (3f). MS *m*/*z* 912 (M^+), 881, 880, and 811. Anal. Calcd for $C_{44}H_{28}F_{12}O_8$: C, 57.90; H, 3.09. Found: C, 57.74; H, 3.21. **3f−I (type I isomer):** ^{19}F NMR δ −62.43 (s). **3f-II (type II isomer):** pale yellow needles, mp 220−255 °C (decomp); ^{1}H NMR δ 3.97 (12H, s), 6.92 (8H, m), and 7.72 (8H, m); ^{13}C NMR δ 52.4 (Me), 122.0 (q, $J = 276$ Hz), 123.0 (m), 128.0, 129.8, 130.8, 135.6, 137.3 (br), and 165.9; ^{19}F NMR δ −62.82 (s); IR (KBr) 1726vs, 1284vs, 1176vs, and 1130vs cm^{-1}. **3f-III (type III isomer):** ^{19}F NMR δ −62.24 (3F, s), −62.47 (3F, q, $J = 10$ Hz), −62.72 (3F, s), and −63.18 (3F, q, $J = 10$ Hz). **3f-IV (type IV isomer):** ^{19}F NMR δ −62.34 (6F, s) and −63.05 (6F, s).

5,6,7,8-Tetracyclohexyl-5,6,7,8-tetrakis(trifluoromethyl)-[4]radialene (3g). MS *m*/*z* 704 (M^+), 622, 540, and 458. **3g-I (type I isomer):** ^{19}F NMR δ −59.84 (s). **3g-II (type II isomer):** colorless crystals, mp 230−232 °C; ^{1}H NMR δ 1.10−

1.35 (12H, m), 1.35−1.60 (12H, m), 1.60−1.85 (16H, m), and 2.53 (4H, br-t, $J = 11.7$ Hz); ^{19}F NMR δ −59.14 (s); ^{13}C NMR δ 25.7, 25.8, 27.1, 28.5, 30.8, 41.8 (CH), 124.1 (q, $J = 30$ Hz), 124.3 (q, $J = 277$ Hz), 124.2 (q, $J = 29$ Hz), 124.3 (q, $J = 277$ Hz), and 136.7 (m). **3g-III (type III isomer):** ^{1}H NMR δ 1.1−2.0 (40H, m) and 2.3−2.6 (4H, m); ^{19}F NMR δ −58.66 (3F, s), −59.13 (3F, s), −59.77 (3F, q, $J = 10$ Hz), and −59.96 (3F, q, $J = 10$ Hz). **3g-IV (type IV isomer):** ^{19}F NMR δ −58.56 (6F, s) and −59.94 (6F, s).

4,5,6-Tricyclohexyl-4,5,6-tris(trifluoromethyl)[3]-radialene (5g). MS m/z 528 (M$^+$), 445, 363, and 321. ***asym*-5g:** waxy solid; ^{1}H NMR δ 1.10−1.45 (10H, m), 1.50−2.10 (21H, m), and 2.26−3.00 (2H, m); ^{19}F NMR δ −56.20 (3F, s) and −58.93 (6F, m); ^{13}C NMR δ 25.5, 25.5, 25.7, 26.5, 26.6 (2C), 30.2, 30.4 (2C), 43.0, 45.6, 45.7, 116.5 (q, $J = 6$ Hz), 117.8 (q, $J = 6$ Hz), 118.7 (q, $J = 6$ Hz), 124.1 (q, $J = 277$ Hz), 124.2 (q, $J = 29$ Hz), 124.3 (q, $J = 277$ Hz), 125.1 (q, $J = 30$ Hz), 126.1 (q, $J = 278$ Hz), and 127.4 (q, $J = 29$ Hz). ***sym*-5g:** ^{19}F NMR δ −56.38 (s).

Photochemical Isomerization of 3. Typical Procedure for Conditions B (Table 3, run 2). The type II isomer **3a-II** (68 mg) and benzene (20 mL) were put in a Pyrex flask, and the vessel was cooled by a flow of water, surrounded by aluminum foil, and irradiated by a 40 W fluorescent lamp. After the indicated time passed, 4 mL of the solution was taken by a syringe and subject to the NMR analysis.

Photochemical Isomerization of 3. Typical Procedure for Conditions A (Table 3, run 1). The type II isomer **3a-II** (125 mg) was put in a vial and dissolved by 10 mL of toluene. The vial was left on a bench. After the indicated time passed, 2 mL of the mixture was taken up, and the solvent was evaporated in vacuo. The residue was dissolved in CDCl$_3$, and the NMR analysis was carried out. After removal of CDCl$_3$ in vacuo, the residue was dissolved in 2 mL of toluene, and the solution was added back to the reaction mixture. After 130 d, toluene was removed to give a nonfluorescent colorless oil, which was chromatographed on silica gel to afford 93 mg (74%) of cyclobuta[*b*]naphthalenes **6A**−**F** in the ratio of 44:27:17:2:6:4. Repeated chromatograpy and fractional recrystallization afforded pure isomers of **6A** and **6C**, structures of which were fully assigned by NMR including H−H, F−F, and C−H COSY spectra. Isomers **6E** and **6F** were isolated by gathering the mother liquors of several experiments followed by repeated chromatography, preparative GPC, and fractional recrystallization.

3-Phenyl-1,2-bis(1-phenyl-2,2,2-trifluoroethylidene)-3,8-bistrifluoromethyl-1,2,3,8-tetrahydrocyclobuta[*b*]-naphthalene (6). MS m/z 680 (M$^+$), 611, 602, and 533. Anal. Calcd for $C_{36}H_{20}F_{12}$: C, 63.54; H, 2.96. Found: C, 63.53; H, 2.99. **6A:** colorless crystals, mp 201−203 °C; ^{1}H NMR (50 °C) δ 5.05 (1H, q, $J = 7.3$ Hz, H^8), 6.51 (2H, br), 6.83 (2H, br), 6.84 (2H, m), 6.86 (1H, d-quint, $J = 7.6$ and 1.5 Hz, H^4), 7.05 (3H, br m), 7.15 (2H, m), 7.18 (1H, ddd, $J = 7.8$, 7.6, and 1.5 Hz, H^5), 7.31 (1H, td, $J = 7.8$ and 1.5 Hz, H^6), 7.37 (5H, m), and 7.51 (1H, br d, $J = 7.8$ Hz, H^7); ^{19}F NMR (50 °C) δ −58.35 (3F, q, $J = 7.5$ Hz, 1-CCF$_3$), −61.81 (3F, s, 2-CCF$_3$), −64.58 (3F, br s, 3-CF$_3$), and −66.04 (3F, quint-d, $J = 7.5$ and 1.5 Hz, 8-CF$_3$); ^{13}C NMR (50 °C) δ 43.3 (qq, $J = 29$ and 6 Hz, C8), 55.6 (q, $J = 26$ Hz, C3), 117.2 (q, $J = 32$ Hz, C1′), 117.5 (q, $J = 33$ Hz, C1′), 121.7 (q, $J = 274$ Hz, CF$_3$), 123.9 (q, $J = 274$ Hz, CF$_3$), 124.6 (q, $J = 286$ Hz, 2 × CF$_3$), 126.2, 127.3, 127.5, 128.0, 128.5, 128.5, 128.9, 129.1, 129.3, 129.4 (br), 130.3, 130.6, 130.8 (m), 130.8 (m), 131.9, 133.0, 134.7, 137.1, 141.6 (q, $J = 4$ Hz, C1 or C2), 142.4 (q, $J = 4$ Hz, C1 or C2), 153.0 (br, C2a or C8a), and 154.0 (br, C2a or C8a); IR (KBr) 1312vs, 1232vs, 1192vs, 1166vs, 1112vs, and 1022vs cm^{-1}. **6B (tentative assignment):** ^{1}H NMR (typical signal) δ 5.07 (1H, q, $J = 7.3$ Hz); ^{19}F NMR δ −58.69 (3F, q, $J = 7$ Hz), −60.71 (3F, q, $J = 11$ Hz), −65.01 (3F, q, $J = 11$ Hz), and −66.34 (3F, quint, $J = 7$ Hz). **6C:** colorless crystals, mp 175−176 °C; ^{1}H NMR (50 °C) δ 3.85 (1H, q, $J = 7.6$ Hz, H^8), 6.4−7.0 (6H, m), 7.0−7.3 (8H, m), and 7.3−7.6 (5H, m); ^{19}F NMR δ −61.05 (3F, q, $J = 14$ Hz, 1- or 2-CCF$_3$), −62.53 (3F, q, $J = 14$ Hz, 1- or 2-CCF$_3$), −64.72 (3F, s, 3-CF$_3$), and −66.03 (3F, d, $J = 7$ Hz, 8-CF$_3$); ^{13}C NMR δ 41.7 (q, $J = 29$ Hz, C8), 55.2 (q, $J = 26$ Hz, C3), 116.1 (q, $J = 33$ Hz, C1′), 118.1 (q, $J = 32$ Hz, C1′), 122.7 (q, $J = 272$ Hz, CF$_3$), 122.7 (q, $J = 274$ Hz, CF$_3$), 123.7 (q, $J = 283$ Hz, CF$_3$), 124.4 (q, $J = 287$ Hz, CF$_3$), 125.8, 127.2 (br), 127.3, 127.4 (br), 127.6, 128.3, 128.3, 128.9, 129.1 (br), 129.2, 129.3, 130.2, 130.4 (br), 130.9, 131.9 (q, $J = 2$ Hz) 132.1, 135.1, 136.7, 141.4 (q, $J = 4$ Hz, C1 or C2), 142.2 (q, $J = 4$ Hz, C1 or C2), 152.8 (br, C2a or C8a), and 153.5 (br, C2a or C8a). **6D (tentative assignment):** ^{1}H NMR (typical signal) δ 4.57 (1H, br q, $J = 7.8$ Hz); ^{19}F NMR δ −60.10 (3F, s), −60.72 (3F, q, $J = 11$ Hz), −65.14 (3F, q, $J = 11$ Hz), and −66.34 (3F, d, $J = 8$ Hz). **6E:** colorless crystals, mp 237−239 °C; ^{1}H NMR δ 5.17 (1H, q, $J = 7.5$ Hz) and 6.2−7.6 (19H, br m); ^{19}F NMR δ −58.76 (3F, q, $J = 7$ Hz), −61.55 (3F, q, $J = 14$ Hz), −63.35 (3F, m), and −63.70 (3F, septet, $J = 14$ Hz). **6F:** colorless crystals, mp 197−199 °C; ^{1}H NMR δ 5.11 (1H, q, $J = 7.8$ Hz), 6.3−7.0 (5H, br m), and 7.0−7.6 (15H, m); ^{19}F NMR δ −58.36 (3F, q, $J = 8$ Hz), −62.09 (3F, s), −63.34 (3F, q, $J = 13$ Hz), and −63.77 (3F, q-quint, $J = 13$ and 8 Hz).

X-ray Analysis. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromator and a 12 kW rotating anode generator. The data were collected at a temperature of 25 ± 1 °C using the ω scan technique. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.18° with a taking-off angle of 6.0°/min (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 2 rescans). An empirical correction for the absorption was made on the basis of azimuthal (Ψ) scans of three reflections.[14] The structure was solved by the direct method (Mithril, SIR, or Multan). The coordinates of the H-atoms were calculated. Calculations were carried out on a VAX station 3200 computer with TEXSAN programs[15] or NEC VM45J/6 with PC-teXsan which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography."[16] **Crystal data for 3e-II:** $C_{60}H_{36}F_{12}$, triclinic, space group *P*-1 (#2), $Z = 2$, $a = 12.912(3)$ Å, $b = 17.290(6)$ Å, $c = 12.927(4)$ Å, $\alpha = 104.50(2)°$, $\beta = 119.96(1)°$, $\gamma = 89.99(2)°$, $V = 2394(2)$ Å^3, $D_c = 1.366$ g·cm^{-1}, dimensions 0.80 × 0.35 × 0.25 mm, Cu Kα, $\mu = 9.28$ cm^{-1}, $F(000) = 1008$, 7814 reflections measured, 7436 of which were unique ($R_{\rm int} = 0.037$). Phenyl groups were treated as restricted groups. All other non-hydrogen atoms were refined anisotropically; $R = 0.065$ and $R_w = 0.076$ for 4255 reflections with $I > 1\sigma(I)$, reflection/parameter = 6.56, GOF = 1.87, $\Delta\rho_{\min} = -0.19$ e·Å^3, $\Delta\rho_{\max} = 0.20$ e·Å^3. **Crystal data for 3a-IV:** $C_{36}H_{20}F_{12}{\cdot}0.5C_7H_8$, monoclinic, space group *C*2/*c* (#15), $Z = 8$, $a = 30.42(1)$ Å, $b = 11.577(3)$ Å, $c = 21.589(2)$ Å, $\beta = 113.33(2)°$, $V = 6982(4)$ Å^3, $D_c = 1.382$ g·cm^{-1}, dimensions 0.30 × 0.28 × 0.22 mm, Mo Kα, $\mu = 1.19$ cm^{-1}, $F(000) = 2952$, 8559 reflections measured, 8396 of which were unique ($R_{\rm int} = 0.166$). The intensity decreased to 77% during the measurement. Fluorine and toluene-carbon atoms were refined anisotropically. The phenyl groups were treated as restricted groups, and toluene was disordered; $R = 0.084$ and $R_w = 0.073$ for 1456 reflections with $I > 2.5\sigma(I)$, reflection/parameter = 6.02, GOF = 1.92, $\Delta\rho_{\min} = -0.37$ e·Å^3, $\Delta\rho_{\max} = 0.64$ e·Å^3. **Crystal data for 4d:** $C_{36}H_{16}Cl_4F_{12}$, triclinic, space group *P*-1 (#2), $Z = 4$, $a = 17.077(2)$ Å, $b = 19.122(3)$ Å, $c = 12.248(1)$ Å, $\alpha = 95.68(1)°$, $\beta = 100.01(1)°$, $\gamma = 114.506(9)°$, $V = 3517.9(8)$ Å^3, $D_c = 1.545$ g·cm^{-1}, dimensions 0.40 × 0.25 × 0.20 mm, Mo Kα, $\mu = 4.25$ cm^{-1}, $F(000) = 1632$, 16671 reflections measured, 16133 of which were unique ($R_{\rm int} = 0.041$). The phenyl carbons were treated as restricted groups, and other non-hydrogen atoms were refined anisotropically; $R = 0.072$ and $R_w = 0.074$ for 4475 reflections with $I > 3\sigma(I)$, reflection/parameter = 7.98, GOF = 2.00, $\Delta\rho_{\min} = -0.44$ e·Å^3, $\Delta\rho_{\max} = 0.61$ e·Å^3. **Crystal data for 6C:** $C_{36}H_{20}F_{12}$, monoclinic, space group $P2_1/c$ (#14), $Z = 4$, $a = 9.433(1)$ Å, $b = 25.193(2)$ Å, $c = 13.154(1)$ Å, $\beta = 98.340(8)°$, $V = 3093.1(5)$ Å^3, $D_c = 1.461$ g·cm^{-1}, dimensions 0.50 × 0.31 × 0.30 mm, Mo Kα, $\mu = 1.29$ cm^{-1}, $F(000) = 1376$, 7693

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[14] G. J. Gilmore, *J. Appl. Crystallogr.* **1984**, *17*, 42.

[15] *TEXSAN−Texray Structure Analysis Package*, Version 5.0; Molecular Structure Corporation: The Woodlands, TX, 1989.

[16] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, Table 2.2 A and 2.3.1

reflections measured, 7272 of which were unique ($R_{int} = 0.023$). All non-hydrogen atoms were refined anisotropically; $R = 0.063$ and $R_w = 0.060$ for 3182 reflections with $I > 2\sigma(I)$, reflection/parameter = 7.35, GOF = 1.68, $\Delta\rho_{min} = -0.30$ e•Å^3, $\Delta\rho_{max} = 0.23$ e•Å^3. **Crystal data for 6F:** $C_{36}H_{20}F_{12}$, triclinic, space group P-1 (#2), $Z = 2$, $a = 10.4365(8)$ Å, $b = 16.295(2)$ Å, $c = 9.886(1)$ Å, $\alpha = 105.086(8)°$, $\beta = 104.097(7)°$, $\gamma = 97.057(7)°$, $V = 1542.9(3)$ Å^3, $D_c = 1.465$ g•cm^{-1}, dimensions 0.55 × 0.35 × 0.25 mm, Cu Kα, $\mu = 11.97$ cm^{-1}, $F(000) = 688.00$, 5097 reflections measured, 4792 of which were unique ($R_{int} = 0.040$). All non-hydrogen atoms were refined anisotropically, and one trifluoromethyl group was disordered; $R = 0.042$ and $R_w = 0.054$ for 3797 reflections with $I > 2.5\sigma(I)$, reflection/parameter = 8.24, GOF = 2.00, $\Delta\rho_{min} = -0.21$ e•Å^3, $\Delta\rho_{max} = 0.23$ e•Å^3.

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Supporting Information Available: Experimental crystallographic details, positional and thermal parameters for **3a-IV**, **3e-II**, **4d**, **6C**, and **6F**. This material is available free of charge via the Internet at http://pubs.acs.org.

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