Synthesis and Structure of 1,4-Dimethoxy and 1,4-Dimethyl-9-(trifluoromethyl)triptycenes

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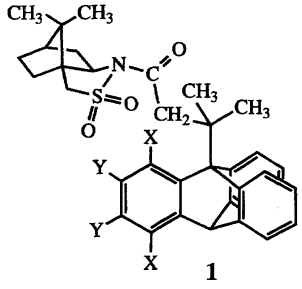
As the first example of triptycenes carrying a trifluoromethyl group at the 9-position, the title compounds were synthesized by the Diels–Alder reaction of 9-(trifluoromethyl)anthracene with a substituted benzyne. Rotational barrier of the 9-trifluoromethyl group is more than 25 kcal mol^{-1} according to the ^{19}F NMR measurements at high temperatures. X-Ray analyses of these compounds reveal that molecules have some unusual bond lengths and angles ascribable to steric interactions between the 1-substituent and the 9-trifluoromethyl group. Comparison of these structural parameters with those of the 9-*t*-alkyltriptycenes reported previously reveals that the out-of-plane bending of the 1-methoxy group in the latter is unusual. We attribute this anomaly to the presence of the C–H···O hydrogen bond.

Recently, X-ray structures of 9-*t*-alkyl-substituted triptycenes with various substituents at the 1—4 positions, compounds **1**[1] and related compounds **2**,[2] have been reported (Chart 1). One of the structural features is that the substituent at the 9-position is bent away from the 1-substituent to avoid the steric interaction. Bending away of the 1-substituent from the 9-substituent was observed except in the dimethoxy compound (**1a**). Compound **1a** showed another unusual feature of conformation: The 1-methoxy group is twisted out of the plane of the benzene ring, whereas the 4-methoxy coplanar. We tentatively concluded that the exceptional features in **1a** could be attributed to an attractive interaction, the C–H···O hydrogen bond between the methoxy-oxygen and hydrogens in the 9-alkyl group. Although the hydrogen bond between a C–H group of a methyl and an ether-oxygen is proposed as an explanation of anomalous population in 9-isobutyl-1,4-dimethoxytriptycene rotamers[3] and in other systems,[4] further works are necessary to understand the contribution of this kind of hydrogen bonds in determining the structure.

One of the strategies to see whether such an interaction is significant or not in the dimethoxytriptycenes is the substitution of an alkyl group having no hydrogen atoms, which can interact with an oxygen atom, for the 9-*t*-alkyl group, with keeping the steric size as constant as possible. If any change in structural parameters should occur by changing the substituent, it should be possible to discuss the presence or absence of such an interaction. A trifluoromethyl group was chosen for the substituent at the 9-position because it bears no hydrogen, although it is sterically smaller than a *t*-butyl group. 1,4-Dimethoxy and 1,4-dimethyl-9-(trifluoromethyl)triptycenes (**3**) were synthesized and their structures analyzed by X-ray crystallography.

Because these compounds are the first examples of triptycene derivatives carrying a trifluoromethyl group at the 9-position, it is also meaningful to investigate the rotational barrier of the 9-CF_3 group on the ground that 9-triptycyl group greatly restricts the rotation of the 9-substituent in 9-substituted triptycenes:[5,6] Compounds **3** are expected to have a very high barrier to the C_9–C_{CF_3} bond rotation. We thus tried to determine the rotational barrier of the CF_3 group by NMR measurements at variable temperatures.



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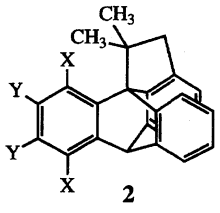

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a X=OCH_3, Y=H
b X=CH_3, Y=H
c X=Y=F
d X=Y=Cl

Chart 1.

Results and Discussion

Synthesis and Rotational Barrier of CF_3 Group. Compounds **3** were synthesized according to the route shown in Scheme 1. 9-(Trifluoromethyl)-anthracene (**5**) was synthesized by trifluoromethylation of 9-iodoanthracene (**4**)[7] with sodium trifluoroacetate in the presence of copper(I) iodide.[8,9] The Diels–Alder reaction of the anthracene with a benzyne, which was generated from an anthranilic acid and isopentyl nitrite, gave the triptycenes **3a** and **3b** in 12 and 23% yields, respectively, with recovery of about 30% of the starting anthracene. The yields are much lower than those for 9-*t*-alkyltriptycenes[10] irrespective to the small steric size of the CF_3 group compared with a *t*-alkyl group. The poor conversion can be attributed to the strongly electron-withdrawing property of the CF_3 group, which lowers the HOMO level of the anthracene moiety.

^{1}H NMR signal due to the 1-methyl group for compound **3b** appeared as a triplet as a result of coupling with the proximate two fluorine atoms. The other proton signals have no observable couplings with fluorines both in **3a** and in **3b**.

^{19}F NMR spectrum of compound **3a** showed a typical A_2B pattern at −55.5 (A_2) and −56.7 (B) ppm with a spin-spin coupling constant of 137 Hz in $CDCl_3$ at room temperature. A similar spectral pattern was observed for the dimethyl compound (**3b**). This means that the rotation around the bond between the carbon at the 9-position and the trifluoromethyl-carbon is frozen on the NMR time scale at the temperature. The A_2 part is assigned to the two fluorine atoms at the synclinal position about the C_9–C_{CF_3} bond and the B part to the one fluorine at the antiperiplaner position.

The A_2B pattern of ^{19}F NMR signals was observed unchanged in the temperature range between the room temperature and 150 °C in DMSO-d_6 for both the compounds. This observation indicates that the rate of C–C bond rotation is less than 1 s^{-1} at the highest temperature observed, the barrier height being at least 25 kcal mol^{-1} (1 cal=4.184 J). Some literatures reported the rotational barrier of CF_3 groups attached to an sp^3 carbon to be 6.1—11.3 kcal mol^{-1}.[11,12] The barrier we estimated for compounds **3** is the highest in the rotational barriers of CF_3 groups to our knowledge. The considerable enhancement of the barrier to rotation is ascribed to the effectiveness of the triptycene moiety in enhancing the rotational barrier as observed for other 9-substituted triptycenes.[5,6]

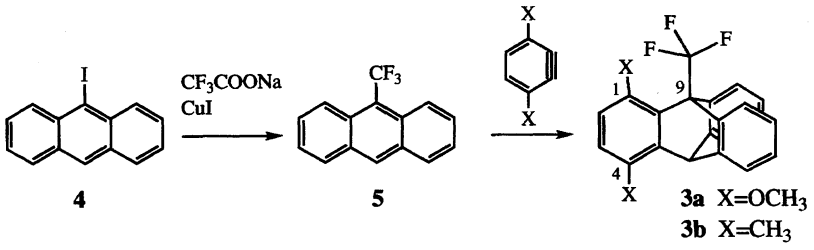
X-Ray Structure. Structures of **3a** and **3b** were analyzed by X-ray crystallography. Final positional and thermal parameters are listed in Table 1 and ORTEP views in Fig. 1. Selected structural parameters are listed in Tables 2 and 3 together with those of triptycenes carrying a *t*-alkyl group at the 9-position (**1a** and **1b**) and related compounds (**2a**) for comparison.

The CF_3 group at the 9-position takes a staggered conformation with respect to the three benzeno groups of the triptycene moiety to avoid the steric repulsion in both the compounds. The C–F bond distances, 1.33—1.38 Å, are typical for that in a trifluoromethyl group.[13] The C(9)–C(17) bond distances are comparable to the C–C bond in 1,1,1-trifluoroethane[13] even though severe steric congestion exists around the bridgehead position.

Bond distances connecting the bridgehead carbon C(9) to the three benzeno carbons in compounds **3** are somewhat longer than a standard value (1.51 Å). The extent of bond lengthening in **3** is smaller than that in the 9-*t*-alkyltriptycenes **1**, this being a reflection of a small steric size of the CF_3 group with respect to the *t*-alkyl group. There are significant bond angle deformations at the C(9) atom in **3**; bond angles are large outside of the triptycene skeleton and small inside. Especially, the C(9a)–C(9)–C(17) angle is larger by ca. 10° than the ideal tetrahedral angle to minimize steric interactions between the 1-substituent and the 9-substituent. These deformations are characteristic for 9-substituted triptycenes.[1—3,14—16]

The nonbonding distances from the 1-substituent to the proximate two fluorines are 2.63 and 2.88 Å for **3a** and **3b**, respectively, apparently smaller than the sum of van der Waals radii of fluorine (1.47 Å) and the 1-substituent, oxygen (1.52 Å) or methyl (1.80 Å).[17] This nonbonding contact causes the long range coupling of the 1-methyl protons with the two fluorine atoms in **3b**.

The bending of the 1-methyl group away from the 9-substituent is still substantial in **3b** as seen from the C(9a)–C(1)–C(18) bond angle in Table 2, although the extent is smaller than in the 9-*t*-alkyl compound (**1b**) because of a small size of the CF_3 group. By contrast, the corresponding bond angle in the dimethoxy compound, C(9a)–C(1)–O(1), is nearly 120°, which is a standard value of an sp^2 carbon, in **3a** as well as in **1a**.



Scheme 1.

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 1,4-Dimethoxy-9-(trifluoromethyl)triptycene (**3a**) and 1,4-Dimethyl-9-(trifluoromethyl)triptycene (**3b**)[a)]

Atom	x	y	z	B_{eq}[b)]
Compound **3a**				
F(1)	0.3992(1)	0.4175(3)	0.6242(2)	7.8(1)
F(2)	0.4678(1)	0.3059(3)	0.6103(2)	7.07(9)
F(3)	0.4222(1)	0.2398(4)	0.7153(2)	7.4(1)
O(1)	0.3251(1)	0.2935(4)	0.6976(3)	7.0(1)
O(2)	0.2539(1)	−0.0913(4)	0.4242(2)	5.9(1)
C(1)	0.3057(2)	0.1995(5)	0.6316(3)	4.8(1)
C(2)	0.2558(2)	0.1555(6)	0.6224(4)	5.2(1)
C(3)	0.2374(2)	0.0609(6)	0.5548(4)	5.2(1)
C(4)	0.2681(2)	0.0057(5)	0.4941(3)	4.4(1)
C(4a)	0.3180(1)	0.0487(5)	0.5012(3)	3.9(1)
C(5)	0.3735(2)	0.1641(8)	0.3006(4)	5.7(2)
C(6)	0.3917(2)	0.293(1)	0.2724(5)	7.5(2)
C(7)	0.4097(2)	0.392(1)	0.3355(7)	7.5(2)
C(8)	0.4114(2)	0.3681(6)	0.4288(5)	5.6(2)
C(8a)	0.3934(1)	0.2359(5)	0.4586(3)	4.2(1)
C(9)	0.3930(1)	0.1818(5)	0.5593(3)	3.9(1)
C(9a)	0.3373(1)	0.1460(5)	0.5697(3)	3.8(1)
C(10)	0.3550(2)	−0.0017(5)	0.4354(3)	4.2(1)
C(10a)	0.3742(2)	0.1360(5)	0.3939(3)	4.5(1)
C(11)	0.3992(1)	−0.0617(5)	0.4966(3)	3.7(1)
C(12)	0.4203(1)	0.0330(5)	0.5622(3)	3.9(1)
C(13)	0.4624(2)	−0.0082(6)	0.6218(4)	5.0(1)
C(14)	0.4813(2)	−0.1478(7)	0.6114(5)	6.1(2)
C(15)	0.4597(2)	−0.2411(7)	0.5473(5)	6.2(2)
C(16)	0.4189(2)	−0.1999(5)	0.4887(4)	5.2(1)
C(17)	0.4193(2)	0.2846(6)	0.6274(4)	5.7(1)
C(18)	0.2937(2)	0.3540(6)	0.7593(4)	7.3(2)
C(19)	0.2036(2)	−0.1461(9)	0.4190(6)	7.1(2)
Compound **3b**				
F(1)	0.2350(4)	0.0912(3)	0.6834(5)	10.3(2)
F(2)	0.3282(5)	0.0549(3)	0.8859(5)	9.6(1)
F(3)	0.3570(5)	0.0018(2)	0.6733(5)	9.0(1)
C(1)	0.6442(8)	0.0264(3)	0.8346(7)	5.8(2)
C(2)	0.7811(9)	0.0199(4)	0.865(1)	6.8(2)
C(3)	0.8693(8)	0.0662(4)	0.816(1)	7.6(3)
C(4)	0.8325(7)	0.1220(3)	0.7392(8)	5.5(2)
C(4a)	0.7001(6)	0.1300(3)	0.7087(6)	4.3(1)
C(5)	0.6074(7)	0.1751(3)	0.3350(7)	5.7(2)
C(6)	0.533(1)	0.1437(5)	0.2217(8)	7.4(3)
C(7)	0.4327(8)	0.1032(4)	0.2567(7)	6.4(2)
C(8)	0.4012(7)	0.0886(4)	0.4098(8)	5.7(2)
C(8a)	0.4762(7)	0.1182(3)	0.5240(6)	4.4(1)
C(9)	0.4644(6)	0.1070(3)	0.7011(7)	4.0(1)
C(9a)	0.6038(6)	0.0835(3)	0.7538(6)	4.0(1)
C(10)	0.6493(7)	0.1896(3)	0.6226(7)	4.6(2)
C(10a)	0.5769(7)	0.1621(3)	0.4860(6)	4.3(1)
C(11)	0.5476(7)	0.2219(3)	0.7266(6)	4.9(2)
C(12)	0.4486(6)	0.1786(3)	0.7709(6)	4.5(1)
C(13)	0.3484(8)	0.1998(4)	0.8716(7)	6.8(2)
C(14)	0.355(1)	0.2663(6)	0.922(1)	9.7(4)
C(15)	0.455(1)	0.3082(5)	0.877(1)	9.5(3)
C(16)	0.5561(9)	0.2877(3)	0.7778(8)	7.3(2)
C(17)	0.3478(8)	0.0657(4)	0.7353(9)	6.8(2)
C(18)	0.559(1)	−0.0295(4)	0.894(1)	10.5(3)
C(19)	0.9359(8)	0.1722(4)	0.689(1)	9.5(3)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/Å^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 2. Selected Structural Parameters in 9-(Trifluoromethyl)-triptycenes, **3a** and **3b**, and 9-*t*-Alkyltriptycenes, **1a** and **1b**[a)]

	3a	**3b**	**1a**[b)]	**1b**[b)]
Bond distances (Å)				
C(1)–X[c)]	1.358(5)	1.50(1)	1.364(4)	1.563(9)
C(4)–Y[d)]	1.378(5)	1.508(10)	1.372(5)	1.507(10)
C(8a)–C(9)	1.546(6)	1.561(8)	1.580(5)	1.571(5)
C(9)–C(9a)	1.552(5)	1.557(8)	1.605(5)	1.599(5)
C(9)–C(12)	1.559(5)	1.555(8)	1.578(5)	1.569(5)
C(9)–C(17)	1.495(7)	1.469(9)	1.580(5)	1.569(5)
C(17)–F(1)	1.364(5)	1.329(9)		
C(17)–F(2)	1.336(6)	1.342(8)		
C(17)–F(3)	1.342(6)	1.383(9)		
Bond angles (°)				
C(9a)–C(1)–X	118.0(4)	127.3(8)	120.6(3)	131.0(5)
C(2)–C(1)–X	123.4(4)	115.7(7)	120.2(3)	111.4(5)
C(3)–C(4)–Y	125.4(4)	119.6(7)	126.3(4)	122.3(6)
C(4a)–C(4)–Y	115.6(4)	123.0(7)	115.3(3)	122.3(6)
C(8a)–C(9)–C(9a)	105.3(3)	105.3(5)	104.4(3)	104.3(3)
C(8a)–C(9)–C(12)	105.2(3)	105.2(5)	101.9(2)	103.1(3)
C(9a)–C(9)–C(12)	105.2(3)	104.7(5)	103.4(2)	104.3(3)
C(8a)–C(9)–C(17)	111.7(4)	110.0(6)	115.2(2)	113.8(3)
C(9a)–C(9)–C(17)	117.6(4)	120.1(5)	116.8(3)	118.4(3)
C(12)–C(9)–C(17)	110.0(4)	110.5(6)	113.3(3)	111.4(3)

a) Values in parentheses are estimated standard deviations. b) Taken from Ref. 1. c) O(1) for the 1,4-dimethoxy compounds and C(18) for 1,4-dimethyl compounds. d) O(2) for the 1,4-dimethoxy compounds and C(19) for 1,4-dimethyl compounds.

Table 3. Comparison of Torsion Angles (°) of Methoxy Groups at the 1- and 4-Positions in 1,4-Dimethoxytriptycene Derivatives[a)]

	3a	**1a**[b)]	**2a**[c)]
C(9a)–C(1)–O(1)–C(18)	177.7(4)	168.4(3)	172.0(3)
C(4a)–C(4)–O(2)–C(19)	175.6(5)	174.9(3)	178.0(3)

a) Values in parentheses are estimated standard deviations. b) Taken from Ref. 1. c) Taken from Ref. 2. Numbering of atoms on this molecule is different but we take the same numbers for the corresponding carbons and the oxygens, for comparison.

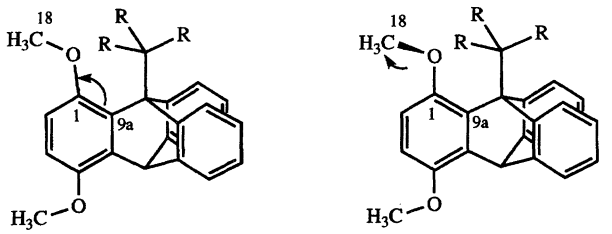
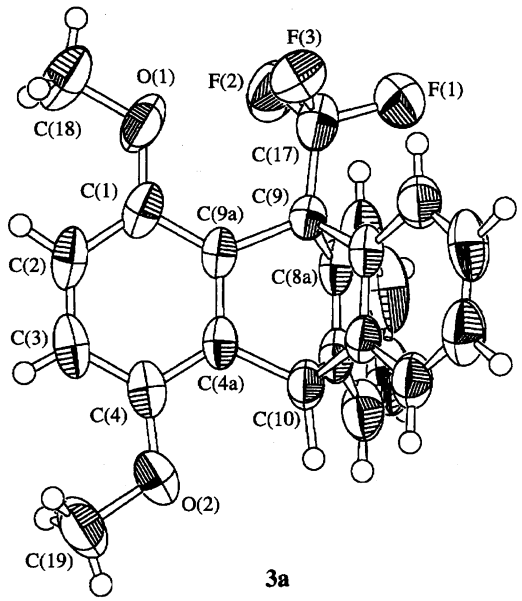


Chart 2.

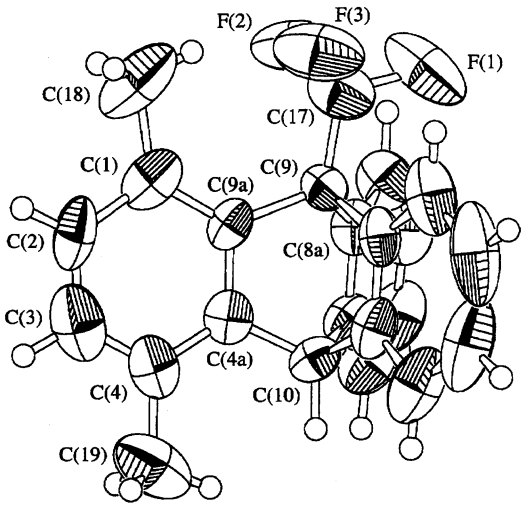
There seems to be two criteria to discuss presence or absence of the proposed C–H···O hydrogen bond. One is the in-plane bond angle deformation concerning the 1-substituent and the other is the out-of-plane deformation of the 1-methoxy group (Chart 2). The former was used to postulate the presence of the C–H···O hydrogen bond in compounds **1a** and **2a** because the 1-methoxy group tends to slightly lean to the 9-substituents or to take a normal bond angle irrespective of the fact that other substituents at the 1-position are bent away from the 9-substituent,[1,2)] and the latter for claiming the presence of charge transfer interaction between the methoxy-oxygen and C–H[3)] or CH_2–Cl group.[4)]

The experimental results about the in-plane deformation concerned with the 1-substituent show that, while the methyl group in **3b** is bent away from the 9-trifluoromethyl group, the methoxy-group in **3a** is not so but takes almost the normal bond angle. If this indication is taken important, then we should conclude that the C–H···O hydrogen bond in compound **1a** or **2a** is not the cause for the normal bond angle but rather, because of the double bond nature of the C_{Ar}–O bond, the bending of the angle is not a favored deformation to relieve the steric strain.

The torsion angle of C(9a)–C(1)–O(1)–C(18) in compound **3a** is very close to 180° and is almost the same with the corresponding angle concerning the 4-methoxy group. By contrast, the same angles in compounds **1a** and **2a** deviate from 180° considerably whereas the angle of the 4-methoxy group is normal. On the steric ground as well as the electronic ground, the torsion is not favorable and thus there must be a reason for this deformation. We wish to attribute this deformation to the formation of the hydrogen bond between the meth-



3a



3b

Fig. 1. ORTEP drawings of 1,4-dimethoxy-9-(trifluoromethyl)triptycene (**3a**) and 1,4-dimethyl-9-(trifluoromethyl)triptycene (**3b**).

yl group in the 9-substituent and the 1-methoxy-oxygen. By rotating the methoxy group out of the benzene plane, the hybridization of the atomic orbitals of the oxygen atom change from sp^2 to sp^3-like, which renders ionization potential of the atom low. This will be favorable to the hydrogen bond formation as were discussed in previous papers.[3,18] Therefore the unusual out-of-plane deformation of the 1-methoxy group can be taken as evidence for the presence of the hydrogen bond.

Summarizing the above discussion, we conclude that if the hydrogen bond is absent, the 1-methoxy group should be coplanar with the benzene ring and the out-of-plane torsion of the group evidences the presence of the O···HC(CH_3) hydrogen bond in compounds **1a** and **2a**. There could be charge-transfer interaction between the methoxy-oxygen and the C–F group in the 9-substituent in **3a** as in 9-chloromethyl-1,4-dimethoxytriptycene.[4] However, this weak interaction is prevented because of the severe steric interactions between the methoxy group and one of the two other fluoro substituents in **3a**, which would be resulted by out-of-plane deformation of the methoxy group. The out-of-plane deformation of the 1-methoxy group in **1a** and **2a** in spite of the severe steric situation is thus evidence for the presence of the C–H···O hydrogen bond in these compounds.

Although we put emphasis on the in-plane bending of the 1-substituent in discussing the presence of the hydrogen bond,[1,2] the better expression should now be that hydrogen-bonding is evidenced by the out-of-plane deformation of the methoxy group. The bond angle C(9a)–C(1)–O(1) is close to 120° irrespective of the presence or absence of the hydrogen bond because the molecule gets resonance stabilization by taking that structure. The larger in-plane bending of halogens in compounds **1c**, **1d**, **2c**, and **2d** irrespective of the presence of the buttressing effect than the corresponding methoxy compounds (**1a** and **2a**) is attributed to the ease of deformation because the conjugation between the halogens with the benzene ring is less effective than the methoxy group.

Experimental

^{1}H NMR spectra were measured on a Varian Gemini-300 spectrometer operating at 300.1 MHz. ^{19}F NMR spectra were measured on a Bruker AMX-400 spectrometer at 376.5 MHz with C_6F_6 as an external standard of which chemical shift was at −162.9 ppm under a condition of proton noise-decoupling. NMR spectra at high temperatures were measured for DMSO-d_6 solutions. Melting points are uncorrected. Elemental analyses were performed by a Perkin–Elmer 240C analyzer.

1,4-Dimethoxy-9-(trifluoromethyl)triptycene (3a). A solution of 1.73 g (7.03 mmol) of 9-(trifluoromethyl)anthracene[8,9] and 1.0 mL (7.4 mmol) of isopentyl nitrite in 150 mL of 2-butanone was refluxed in a three-necked flask. To the solution were added a solution of 4.28 g (21.7 mmol) of 3,6-dimethoxyanthranilic acid[19] in 50 mL of 2-butanone and a solution of 2.9 mL (22 mmol) of isopentyl nitrite in 50 mL of 2-butanone from respective dropping funnels in 2 h. The mixture was refluxed for additional 2 h. The volatile materials were evaporated under reduced pressure and the residue was chromatographed on alumina (eluent hexane–dichloromethane 4:1). Recrystallization from hexane gave 0.32 g (12%) of the desired compound as colorless crystals and 27% of the starting anthracene was recovered. Mp 254.5—255.5 °C. Found: C, 72.29; H, 4.48%. Calcd for $C_{23}H_{17}F_3O_2$: C, 72.24; H, 4.48%. ^{1}H NMR ($CDCl_3$) δ=3.77 (3H, s), 3.82 (3H, s), 5.91 (1H, s), 6.63 (2H, s), 7.04—7.07 (4H, m), 7.44 (2H, m), 7.66 (2H, m). ^{19}F NMR ($CDCl_3$) δ=−55.5 (2F, A_2 part of the A_2B, J=137 Hz), −56.7 (1F, B part of the A_2B, J=137 Hz).

1,4-Dimethyl-9-(trifluoromethyl)triptycene (3b). This compound was similarly prepared from the anthracene

and 3,6-dimethylanthranilic acid.[20] Yield was 23%, and 32% of the starting material was recovered. Mp 212.0—212.5 °C. Found: C, 78.75; H, 4.85%. Calcd for $C_{23}H_{17}F_3$: C, 78.84; H, 4.89%. ^{1}H NMR ($CDCl_3$) δ=2.50 (3H, s), 2.55 (3H, t, J=3.6 Hz), 5.65 (1H, s), 6.76 and 6.78 (2H, ABq, J=7.9 Hz), 7.04—7.10 (4H, m), 7.41 (2H, m), 7.64 (2H, m). ^{19}F NMR ($CDCl_3$) δ=−56.6 (2F, A_2 part of the A_2B, J=125 Hz), −61.3 (1F, B part of the A_2B, J=125 Hz).

X-Ray Crystallography.[21] Crystals used for the measurement were grown from hexane solutions and their sizes were ca. 0.2×0.2×0.3 mm^3. X-Ray measurements were performed on a Rigaku AFC7R four circle diffractometer with Cu $K\alpha$ radiation (λ=1.544178 Å). The reflection data were collected by the ω–2θ method in the range of 2θ< 120° at 16° min^{-1} ratio. The scan range was calculated by 1.78°+0.30°tanθ and 1.15°+0.30°tanθ for compounds **3a** and **3b**, respectively. The structure was solved by the direct method and refined by the full-matrix least-squares method by TEXAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. All hydrogen atoms were found in e-maps and the positional and thermal parameters of some hydrogens were fixed during the refinement. The function minimized was $\Sigma[w(|F_o|-|F_c|)^2]$, where $w=(\sigma_c^2|F_o|)^{-1}$. Crystal and analysis data are as follows.

3a: Formula $C_{23}H_{17}F_3O_2$, F.W. 382.38, monoclinic, $C2/c$ (#15), a=26.806(2), b=9.263(3), c=14.522(3) Å, β=96.01(1)°, V=3586(1) Å^3, Z=8, D_c=1.42 g cm^{-3}, μ=9.34 cm^{-1}, R=0.085, R_w=0.068 for 2118 reflections within $|F_o|>\sigma(F_o)$.

3b: Formula $C_{23}H_{17}F_3$, F.W. 350.38, orthorhombic, $P2_12_12_1$ (#19), a=10.131(7), b=19.87(1), c=8.699(4) Å, V=1751(1) Å^3, Z=4, D_c=1.33 g cm^{-3}, μ=8.17 cm^{-1}, R=0.057, R_w=0.047 for 1215 reflections within $|F_o|>\sigma(F_o)$.

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21) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, complete F_o-F_c data, and all bond distances and angles are deposited as Document No. 68052 at the Office of the Editor of Bull. Chem. Soc. Jpn.