Synthesis and Conformation of 2-Aminophenyldiarylperfluoroalkylmethanes (Molecular Propellers)

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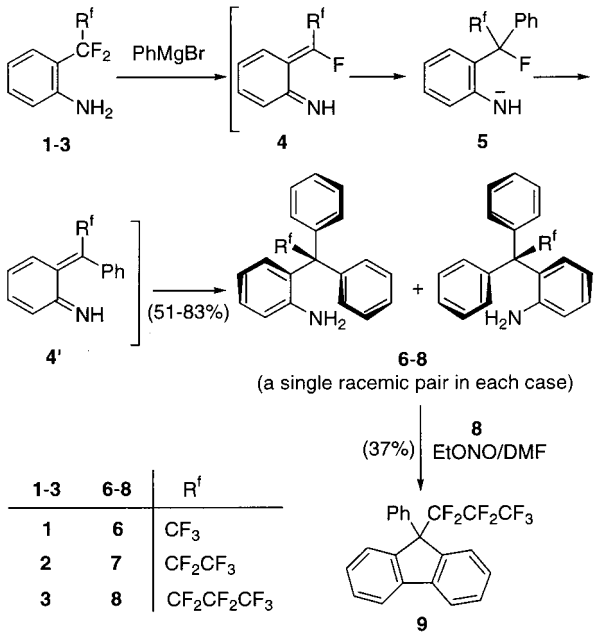
Introduction

Molecular propellers, such as triarylmethanes, exist in chiral helical conformations in which the helicity and the correlated rotation of the planar substituents (blades) are imposed by severe steric hindrance in the molecule (see **6**−**8** in Scheme 1). Depending on the nature of the aryl groups, a single molecule may exist in a large number of conformational isomers.[1,2] Studies on molecular propellers were pioneered by Mislow in the early 1970s, and his fundamental work resulted in an understanding of conformational transitions of this complex class of molecules.[1a] Here, we report a simple synthetic route to perfluoroalkyl-substituted triarylmethanes such as **6**−**8** (Scheme 1) and conformational studies of this previously unknown class of molecular propellers. The easy availability of a series of compounds substituted with a 2-aminophenyl moiety permitted a critical examination of two controversial proposals. Specifically, a stabilizing intramolecular interaction between the amino group and the perfluoroalkyl substituent[3] and the intramolecular hydrogen bonding of the amino group to the π-electron system of the phenyl group have been suggested for related molecules.[1e]

Synthesis

The starting materials **1**−**3** for the synthesis of **6**−**8** are readily available by a coupling reaction of 2-iodoaniline with a perfluoroalkyl iodide in the presence of copper bronze[4] or by reductive perfluoroalkylation of aniline with a perfluoroalkyl iodide in the presence of Zn and SO_2.[5] The former method was used in this work. The treatment of **1**−**3** with phenylmagnesium bromide furnished the respective compounds **6**−**8** in yields of 51−83%. These are isolated yields, and the lowest efficiency of 51% for the relatively volatile CF_3 derivative **6** is due to its partial loss during workup and purification.

Scheme 1



1-3	6-8	R^f
1	6	CF_3
2	7	CF_2CF_3
3	8	$CF_2CF_2CF_3$

The mechanistic pathway to **6**−**8** is a particular case of the chemistry of the anionically activated perfluoroalkyl group.[6,7] Briefly, experimental evidence has been accumulating that the anion derived from **1**−**3** undergoes elimination of fluoride to generate an intermediate product **4** which is then aromatized in the addition reaction with a nucleophile. In the pathway leading to **6**−**8**, the anionic adduct **5** undergoes a similar sequence of the elimination/addition reactions with the intermediary of **4′** to give, after quenching the mixture with water, the final product **6**−**8**.

An attempt was made to deaminate **8** to a triphenylmethyl derivative by treatment with EtONO in DMF.[8] Instead of the expected formal replacement of the amino group by hydrogen, this reaction resulted in deaminative cyclization with the formation of a fluorene **9**. A driving force for this cyclization is a close proximity of the intermediate phenyl cation or radical[8] to the phenyl group in the sterically congested molecular propeller.

A reaction leading to a heteroaryl analogue of **8** is given in Scheme 2. Thus, the treatment of **3** with 2-thienyl-

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(1) For reviews, see: (a) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (b) Eliel, E. L.; Wilen, S. H.; Mander, L. N.; *Stereochemistry of Organic Compounds*; Wiley: New York, 1994. (c) Oki, M. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1983. (d) Oki, M. In *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; Marchand, A. P., Ed.; VCH: Deerfield Beach, 1985. (e) Oki, M. In *The Chemistry of Rotational Isomers*; Hafner, K., Rees, C. W., Trost, B. M., Lehn, J.-M., Schleyer, P. v. R., Zahradnik, R., Eds.; Springler-Verlag: Berlin, 1993.

(2) When the aryl rings are on a double bond, a "vinyl propeller" results: Gur, E.; Kaida, Y.; Okamoto, Y.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1992**, *57*, 3689.

(3) (a) Howard, J. A. K.; Hoy, V. J.; O'Hagen, D. H.; Smith, G. T. *Tetrahedron* **1996**, *52*, 12613. (b) Kovacs, A.; Hargittai, I. *Int. J. Quantum Chem.* **1997**, *62*, 646.

(4) Fuchikami, T.; Ojima, I. *J. Fluorine Chem.* **1983**, *22*, 541. (b) Yoshino, N.; Kitamura, M.; Seto, T.; Shibata, Y.; Abe, M.; Ogino, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2141.

(5) (a) Tordeux, M.; Langlois, B.; Wakselman, C. J. *Chem. Soc., Perkin Trans. 1* **1990**, 2293. (b) Strekowski, L.; Hojjat, M.; Patterson, S. E.; Kiselyov, A. S. *J. Heterocycl. Chem.* **1994**, *31*, 1413.

(6) For reviews, see: Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1978**, *11*, 197. (b) Strekowski, L.; Kiselyov, A. S. *Trends Heterocycl. Chem.* **1993**, *73*, 3. (c) Kiselyov, A. S.; Strekowski, L. *Org. Prep. Proc. Int.* **1996**, *28*, 289.

(7) (a) Strekowski, L.; Lin, S.-Y.; Lee, H.; Mason, J. C. *Tetrahedron* Lett. **1996**, *27*, 4655. (b) Strekowski, L.; Lin, S.-Y.; Lee, H.; Zhang, Z.-Q.; Mason, J. C. *Tetrahedron* **1998**, *54*, 7942.

(8) Doyle, M. P.; Dellaria, J. F.; Siegfried, B.; Bishop, S. W. *J. Org. Chem.* **1977**, *42*, 3494.

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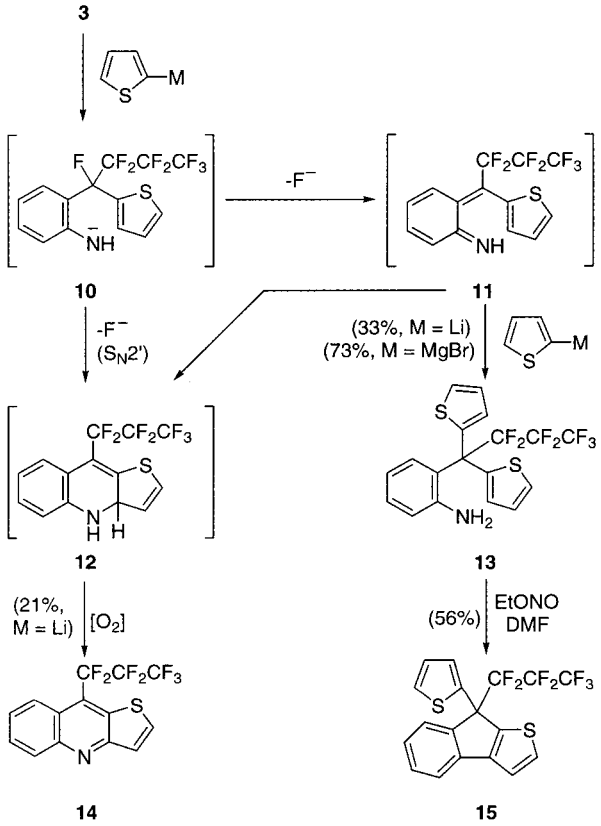
Scheme 2



lithium gave a mixture of the desired compound **13** and a thieno[3,2-*b*]quinoline **14** in a ratio of 3:2 and a total yield of 54%. Products **13** and **14** were separated by chromatography. In the unified mechanism for **13** and **14** it is suggested that the initial adduct **10** can undergo a dual elimination of fluoride ion. The elimination through the benzene moiety, as discussed above, generates **11**, which is a precursor to **13**. This reaction is accompanied by an S_N2' substitution of fluoride ion with the involvement of the thiophene ring in **10**, which results in cyclization to **12**. Alternatively, **12** may be generated by electrocyclization of **11**. The intermediate product **12** is apparently oxidized (aromatized) to **14** by molecular oxygen during workup.

The yield of **13** was improved to 73% by conducting the reaction of **3** with 2-thienylmagnesium bromide instead of 2-thienyllithium. The formation of **14** was completely suppressed in the Grignard reaction. The treatment of **13** with EtONO in DMF resulted in deaminative cyclization to give **15**.

Conformational Studies

The three fluorine atoms of the CF_3 group of **6** are anisochronous at −20 °C, and they give rise to a clearly defined AA′X absorption pattern. As the temperature is raised, the spectrum gradually broadens and then coalesces at 21 °C. In a similar way, AB-type signals observed at −15 °C for the difluoromethylene moiety of **7** coalesce at 43 °C, analogous resonances at 25 °C for each of two sets of geminal fluorines of **8** coalesce to two independent broad signals at 81 °C, and the two AB-type resonances for **13** at −5 °C become broad singlets as the temperature is increased to 35 °C. Due to the large values of coupling constants for geminal fluorines in **7** and **8** ($J \geq 280$ Hz), the relatively weak 1−2 and 1−3 interactions ($J \sim 10$ Hz) cause only a slight broadening of the corresponding signals in the chemical shift scale of ^{19}F NMR. The only exception is a dithienyl derivative **13**, for which even at −60 °C the individual signals are much broader than those for its diphenyl analogue **8**. This result is consistent with an increased conformational complexity of **13**, which is due to two possible, syn and anti, relative orientations of the 2-thienyl groups in the molecular propeller. Indeed, the AB-type signals for the diastereotopic difluoromethylene moieties in the cyclized product **15** are narrow in the tested range of temperatures from −60 to +80 °C and comparable in shape to those for **7** and **8**. The geminal fluorine atoms of the achiral phenyl analogue **9** are isochronous at −60 °C. This important result implies that the temperature-dependent anisochronism of the perfluoroalkyl substituents in **6**−**8** and **13** is mainly due to location of these groups in a chiral environment of the molecular propeller, rather than their restricted rotation. Consistent with this suggestion are small rotation barriers, typically 5−7 kcal/mol reported previously for perfluoroalkyl groups in highly congested molecules.[9] By comparison, the barriers for conformational changes based on the disappearance of diastereotopicity for the perfluoroalkyl moieties were calculated in this work as follows: **6**, 12 kcal/mol; **7**, 14 kcal/mol; **8**, 15 kcal/mol; and **13**, 13 kcal/mol. These values were obtained by using the coalescence data discussed above.[10] The estimated error is ±0.5 kcal/mol.[10c]

The observed single AA′X pattern for CF_3 of **6**, one AB system for geminal fluorines in **7**, and two AB absorptions for **8** are consistent with the presence of a single racemic pair in each case. This is an unusual finding because two racemic pairs, due to two different orientations of the aminophenyl moiety relative to the perfluoroalkyl group in the molecular propeller (syn and anti), can be predicted.[1]

To obtain a better insight into the preferred conformation of these molecular propellers, additional studies with the selected compound **7** were conducted. The UV spectrum taken in hexane shows absorptions at λ_{max} 244 nm (ϵ 10 000) and λ_{max} 298 nm (ϵ 3900) that can safely be assigned to the respective E_2- and B-band. By comparison, the respective B-band in the UV spectra of aniline and *o*-toluidine, taken in hexane, is at λ_{max} 291 nm (ϵ 2500) and λ_{max} 289 nm (ϵ 3200). The bathochromically shifted B-band of **7** is indicative of strong conjugation between the nonbonding electrons on the nitrogen atom and the aromatic π-electron system in the aniline portion of the molecule.[11] It can be suggested that the nitrogen atom acquires sp^2-hybridization that flattens the aniline moiety and which, in turn, minimizes steric hindrance within the molecular propeller.

The IR spectra of **7** taken in the solid state (KBr) and in 0.7 and 0.07 M solutions in CCl_4 all show virtually identical absorptions for NH_2 at 3402 ± 1 cm^{-1} and at 3498 ± 1 cm^{-1}. The absorption bands are relatively strong, symmetric, and narrow with a half-width of approximately 50 cm^{-1}. These results clearly demonstrate

(9) Weigert, F. J.; Mahler, W. *J. Am. Chem. Soc.* **1972**, *94*, 5314.
(10) (a) Kurland, R. J.; Rubin, M. B.; Wise, W. B. *J. Chem. Phys.* **1964**, *40*, 2426. (b) Oki, M.; Iwamura, H.; Hayakawa, N. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1865. (c) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.
(11) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.

the lack of any intermolecular hydrogen bonding interaction of the amino group. They also strongly argue against the *intramolecular* $NH_2\cdots Ph$ hydrogen bonding that has been suggested previously for sterically crowded molecules.[1e]

Since the IR spectra of **7** taken in solution and the solid state are identical, the solid-state structure appears to be an excellent approximation of the conformation in solution. Accordingly, the X-ray diffraction analysis for **7** was conducted (Figure 1, Supporting Information). To the best of our knowledge, this is the first X-ray structure of a triarylmethane that contains a 2-aminophenyl moiety.

In the solid state, the molecule is chiral and adopts a single conformation with the amino group and the perfluoroalkyl substituent anti to each other. The short distance of 1.38 Å for the C−N bond indicates sp^2 hybridization of the nitrogen atom, as obtained from UV studies in solution. The three aryl groups are essentially planar, and distances between the adjacent carbon atoms in the two unsubstituted phenyl rings (1.375 ± 0.019 Å) are in the normal range. By contrast, the C(1)−C(2) bond of the aniline moiety is elongated to 1.42 Å, which minimizes steric interactions of the amino group. The $C-CF_2-CF_3$ subunit is in an almost ideal all-staggered conformation. On the other hand, the molecular propeller is highly distorted as quantified by the following torsion angles with the $C(F_2)$−C(central) bond taken as a reference: 171.8° for $C(F_2)-C-C(1\text{-}PhNH_2)-C(2\text{-}PhNH_2)$ and 108.0° and 116.8° for the analogous chains $C(F_2)-C-C(1\text{-}Ph)-C(2\text{-}Ph)$. Again, the unusually large twist of the aminophenyl moiety minimizes steric interactions of the amino group with the adjacent phenyl rings. A similar conformation in solution should result in a relatively low energy barrier for racemization, as observed. Specifically, the high torsion angle $C(F_2)-C-C(1\text{-}PhNH_2)-C(2\text{-}Ph\text{-}NH_2)$ approximates that of 180 ° in the transition state for racemization of **7** by a one-ring flip mechanism.[1a]

Conclusions

The results of the solution and X-ray crystallographic studies of **7** complement each other and demonstrate that the molecule exists in essentially identical conformations in solution and in the solid state. No unusually short distances between nonbonded atoms in the molecule were found by the X-ray crystallographic analysis. The molecule adopts a distorted helical conformation in which repulsive steric interactions including the $NH_2\cdots Ph$ interactions are minimized. This finding positively rules out the controversial $NH_2\cdots Ph$ hydrogen bonding that has been suggested previously for closely related molecules. An additional argument strongly supporting this conclusion was obtained by molecular modeling. Thus, lowering the distortion of the molecular propeller by rotating the aminophenyl substituent while maintaining the remaining conformational parameters intact greatly increases distances of the aminophenyl moiety to C_2F_5 and one of the phenyl rings and, at the same time, brings the amino group to a closer proximity to the second phenyl ring. This conformation is not observed because the interaction $NH_2\cdots Ph$ is repulsive, not stabilizing.

Experimental Section

General Methods. THF was distilled from sodium benzophenone ketyl immediately before use. All reactions were conducted under an atmosphere of nitrogen. Crude mixtures were analyzed and mass spectra of pure components were obtained on a GC-MS instrument equipped with an on-column injector, a poly(dimethylsiloxane)-coated capillary column, and a mass selective detector operating at 70 eV. Melting points (Pyrex capillary) are uncorrected. The standard ^{1}H NMR (400 MHz) and ^{19}F NMR (282 MHz) spectra were taken at 25 °C in $CDCl_3$ solutions with TMS and C_6F_6 as the respective internal references. H−H coupling constants smaller than 2 Hz are not reported. In the chemical shift scale of ^{19}F NMR the small F−F vicinal coupling constants for a perfluoroalkyl group ($J \sim 10$ Hz) result in only a slight broadening of signals. As such, these coupling constants are not reported as well.

2-Perfluoroalkylanilines 1−3. 2-Iodoaniline was allowed to react with a perfluoroalkyl iodide in the presence of copper bronze in DMF by using a general procedure.[4a] Products **1**−**3** were purified by distillation on a Kugelrohr (80−110 °C/1.5 mmHg) and found to be at least 96% pure by GC.

2-Pentafluoroethylaniline (1): yield 54%; an oil; ^{1}H NMR δ 4.28 (bs, exchangeable with D_2O, 2H), 6.78 (d, J = 8 Hz, 1H), 6.88 (t, J = 8 Hz, 1H), 7.36 (d, J = 8 Hz, 1H), 7.42 (t, J = 8 Hz, 1H); ^{19}F NMR δ 48.5 (2F), 76.8 (3F); HRMS exact mass calcd for $C_8H_6F_5N$ 211.0420, found 211.0418.

2-Heptafluoropropylaniline (2): yield 58%; an oil; ^{1}H NMR δ 4.24 (bs, exchangeable with D_2O, 2H), 6.70 (d, J = 8 Hz, 1H), 6.81 (t, J = 8 Hz, 1H), 7.28 (d, J = 8 Hz, 1H), 7.32 (t, J = 8 Hz, 1H); ^{19}F NMR δ 35.2 (2F), 52.2 (2F), 81.7 (3F); HRMS exact mass calcd for $C_9H_6F_7N$ 261.0388, found 261.0380.

2-Nonafluorobutylaniline (3): yield 88%; an oil; the NMR data were virtually identical with those reported.[4b]

Reactions of 1−3 with Organometallic Reagents. General Procedure. A solution of a Grignard or lithium reagent (10 mmol) in THF (25 mL) was stirred at −70 °C and treated dropwise with a solution of a 2-perfluoroalkylaniline **1**−**3** (3 mmol) in THF (10 mL). Then the mixture was allowed to reach 23 °C within 1 h and stirred at 23 °C for an additional 1 h before being quenched with water. Standard workup was followed by chromatography on silica gel eluting with hexanes/ether (9:1). Products **6**−**9** and **13**−**15** were crystallized from pentanes and ether, respectively.

2-(2,2,2-Trifluoro-1,1-diphenylethyl)aniline (**6**, from **1** and PhMgBr): yield 51%; mp 92−93 °C; ^{1}H NMR δ 3.17 (bs, exchangeable with D_2O, 2H), 6.55 (d, J = 8 Hz, 1H), 6.75 (t, J = 8 Hz, 1H), 7.15 (t, J = 8 Hz, 1H), 7.25 (d, J = 8 Hz, 1H), 7.33 (m, 6H), 7.43 (m, 4H); ^{19}F NMR ($CDCl_3$, −60 °C, AA′X) δ 99.4 (dd, J = 125 and 115 Hz, 1F), 103.3 (d, J = 115 Hz, 1F), 103.7 (d, J = 125 Hz, 1F); ^{19}F NMR ($CDCl_3$, 21 °C, coalescence) δ 102.5 (bs); MS m/z 211 (100), 231 (40, M^+). Anal. Calcd for $C_{20}H_{16}F_3N$: C, 73.38; H, 4.93; N, 4.28. Found: C, 73.44; H, 4.82; N, 4.18.

2-(2,2,3,3,3-Pentafluoro-1,1-diphenylpropyl)aniline (**7**, from **2** and PhMgBr): yield 72%; mp 98−99 °C; ^{1}H NMR δ 3.20 (bs, exchangeable with D_2O, 2H), 6.51 (d, J = 8 Hz, 1H), 6.78 (t, J = 8 Hz, 1H), 7.15 (t, J = 8 Hz, 1H), 7.32 (m, 7H), 7.58 (m, 4H); ^{19}F NMR ($CDCl_3$, −15 °C, AB for CF_2) δ 60.5 (d, J = 280 Hz, 1F), 60.9 (d, J = 280 Hz, 1F), 87.8 (s, 3F); ^{19}F NMR ($CDCl_3$, 43 °C, coalescence) δ 61.7 (bs, 2F), 88.0 (s, 3F); MS m/z 180 (100), 258 (40), 377 (70, M^+). Anal. Calcd for $C_{21}H_{16}F_5N$: C, 66.84; H, 4.27; N, 3.71. Found: C, 66.61; H, 4.07; N, 3.62.

2-(2,2,3,3,4,4,4-Heptafluoro-1,1-diphenylbutyl)aniline (**8**, from **3** and PhMgBr): yield 83%; mp 108−110 °C; ^{1}H NMR δ 3.19 (bs, exchangeable with D_2O, 2H), 6.54 (d, J = 8 Hz, 1H), 6.82 (t, J = 8 Hz, 1H), 7.18 (t, J = 8 Hz, 1H), 7.34 (m, 7H), 7.54 (m, 2H), 7.64 (m, 2H); ^{19}F NMR (DMSO-d_6, 25 °C, 2AB for CF_2-CF_2) δ 43.9 (d, J = 285 Hz, 1F), 49.1 (d, J = 285 Hz, 1F), 63.2 (d, J = 290 Hz, 1F), 66.8 (d, J = 290 Hz, 1F), 82.2 (s, 3F); ^{19}F NMR (DMSO-d_6, 81 °C, coalescence) δ 46.3 (bs, 2F), 65.8 (bs, 2F), 82.5 (s, 3F); MS m/z 180 (100), 258 (50), 427 (40, M^+). Anal. Calcd for $C_{22}H_{16}F_7N$: C, 61.83; H, 3.75; N, 3.28. Found: C, 61.69; H, 3.60; N, 3.22.

2-[2,2,3,3,4,4,4-Heptafluoro-1,1-(2-dithienyl)butyl]-aniline (13): yield 33% from **3** and 2-thienyllithium; yield 73% from **3** and 2-thienylmagnesium bromide; mp 83−85 °C; ^{1}H NMR δ 2.80 (bs, exchangeable with D_2O, 2H), 6.61 (d, J = 8 Hz, 1H), 6.82 (t, J = 8 Hz, 1H), 7.02 (dd, J = 5.2, 3.6 Hz, 2H), 7.20 (t, J = 8 Hz, 1H), 7.35 (m, 4H), 7.46 (bd, J = 8 Hz, 1H); ^{19}F NMR ($CDCl_3$, −5 °C, 2AB for CF_2CF_2) δ 42.2 (bd, J = 280 Hz, 1F), 45.4 (bd, J = 280 Hz, 1F), 57.5 (bd, J = 280 Hz, 1F), 62.0 (bd, J

= 280 Hz, 1F), 80.2 (s, 3F); ^{19}F NMR ($CDCl_3$, 35 °C, coalescence) δ 43.8 (bs, 2F), 59.5 (bs, 2F), 80.3 (s, 3F); MS *m*/*z* 270 (100), 439 (40, M^+). Anal. Calcd for $C_{18}H_{12}F_7NS_2$: C, 49.20; H, 2.75; N, 3.19. Found: C, 49.26; H, 2.72; N, 3.04.

9-Heptafluoropropylthieno[3,2-*b*]quinoline (**14**, from **3** and 2-thienyllithium): yield 21%; mp 72−73 °C; ^{1}H NMR δ 7.67 (t, J = 8 Hz, 1H), 7.69 (d, J = 8 Hz, 1H), 7.83 (t, J = 8 Hz, 1H), 8.00 (d, J = 6 Hz, 1H), 8.29 (m, 2H); ^{19}F NMR δ 37.4 (s, 2F), 57.0 (s, 2F), 81.8 (s, 3F); MS *m*/*z* 234 (100), 353 (50, M^+). Anal. Calcd for $C_{14}H_6F_7NS$: C, 47.60; H, 1.71; N, 3.96. Found: C, 47.66; H, 1.76; N, 3.92.

Deaminative Cyclization of 8 and 13. A solution of **8** or **13** (1 mmol) and EtONO (1.5 mmol) in DMF (30 mL) was heated to 80 °C for 2 h and then cooled to 23 °C and quenched with aqueous HCl (20%, 10 mL). The mixture was extracted with ether (3 × 25 mL), and the extract was dried ($MgSO_4$) and concentrated. Silica gel chromatography (pentanes/ether, 3:1) followed by crystallization from ether gave **9** or **15**.

9-Heptafluoropropyl-9-phenylfluorene (**9**, from **8**): yield 37%; mp 64−66 °C; ^{1}H NMR δ 7.22 (m, 3H), 7.32 (t, J = 8 Hz, 2H), 7.39 (m, 2H), 7.45 (t, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.77 (d, J = 8 Hz, 2H); ^{19}F NMR δ 40.6 (s, 2F), 56.8 (s, 2F), 80.9 (s, 3F); MS *m*/*z* 241 (100), 412 (10, M^+). Anal. Calcd for $C_{22}H_{13}F_7$: C, 64.40; H, 3.17. Found: C, 64.43; H, 3.07.

8-Heptafluoropropyl-8-(2-thienyl)indeno[2,3-*b*]thiophene (**15**, from **13**): yield 56%; mp 23−25 °C; ^{1}H NMR δ 6.95 (dd, J = 5.2, 4.0 Hz, 1H), 7.23 (m, 2H), 7.29 (m, 2H), 7.42 (t, J = 8 Hz, 1H), 7.52 (m, 2H), 7.79 (bd, J = 8 Hz, 1H); ^{19}F NMR δ 38.3 (d, J = 285 Hz, 1F), 40.9 (d, J = 285 Hz, 1F), 53.0 (d, J = 282 Hz, 1F), 55.5 (d, J = 282 Hz, 1F), 80.7 (s, 3F); MS *m*/*z* 253 (100), 422 (40, M^+). Anal. Calcd for $C_{18}H_9F_7S_2$: C, 51.18; H, 2.13. Found: C, 51.49; H, 2.46.

Determination of the Rotation Barriers. The rotation barriers (the free energies of activation, $\Delta G^{\ddagger}$) for **6**−**8** and **13** were derived from temperature-dependent ^{19}F NMR spectra (282 MHz) at the coalescence temperatures. The equations[10a,b] used for the determination of the barriers and a detailed analysis of the accuracy of the determination are given in the excellent treatise by Sandström.[10c] Errors in $\Delta G^{\ddagger}$ for **6**−**8** and **13** were evaluated to be ±0.5 kcal/mol.

X-ray Crystal Structure for 7. A chiral crystal of dimensions 0.476 × 0.408 × 0.204 mm was mounted on thin glass fiber with epoxy cement. Data were collected on a Bruker 1K CCD diffractometer using Mo Kα radiation (0.710 73 A) at 293 K. The material crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.4598(3) Å, b = 12.8487(2) Å, c = 14.4550(5) Å, and Z = 4. Data collection, reduction, solution, and refinement were all carried out using Bruker AXS software.[12] All non-H atoms were refined anisotropically; 2522 observations, 260 variables; R_1 = 0.032 for $F_2 > 4\sigma(F_2)$ and wR_2 = 0.066 for all F_2.

Chirality of 7. Racemic compound **7** crystallizes from pentane in two enantiomorphic crystals and, as shown by X-ray crystallographic analysis, the crystals are composed of single enantiomers of **7**. By mimicking the early work by Pasteur on tartaric acid, it was possible to separate manually the two enantiomorphic sets. Due to the low racemization barrier of 14 kcal/mol, no CD signal for **7** in solution was observed (pentanes, 23 °C, total time of 5 min for the preparation of the solution and analysis).

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Supporting Information Available: Temperature-dependent ^{19}F NMR spectra of **6**−**8** and **13**, full crystallographic data for **7**, and different ORTEP perspectives of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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