Host-Guest Complexation. 26. Cavitands Composed of Fluorobenzene Units Bonded in Their 2,6-Positions To Form Macrocycles[1]

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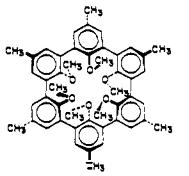
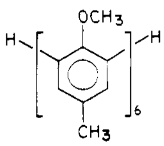
Abstract: Linear and cyclic oligomers of fluorobenzene or 4-methylfluorobenzene units attached to one another at their 2,6-positions are reported. The linear oligomers composed of fluorobenzene units are referred to as $H(C_6H_3F)_nH$, and the cyclic oligomers as $(C_6H_3F)_n$. The linear oligomers composed of 4-methylfluorobenzene units are referred to as $H(CH_3C_6H_2F)_nH$, and the cyclic oligomers as $(CH_3C_6H_2F)_n$. The crystal structure of $(CH_3C_6H_2F)_6$ shows the compound to have approximately D_{3d} symmetry, the fluorine atoms being octahedrally arranged about a cavity of 1.48-Å diameter. The ^{19}F and ^1H NMR spectra of $(CH_3C_6H_2F)_8$ show the compound to have D_{2d} symmetry, the fluorine atoms lining a cavity that in Corey-Pauling-Koltun molecular models is roughly cylindrical, and about 2.7 Å in diameter and 2.7 Å in depth. New linear oligomers synthesized and characterized were $H(C_6H_3F)_3H$, $H(C_6H_3F)_4H$, $H(C_6H_3F)_6H$, $H(C_6H_3F)_8H$, $H(CH_3C_6H_2F)_2H$, $H(CH_3C_6H_2F)_3H$, $H(CH_3C_6H_2F)_4H$, $H(CH_3C_6H_2F)_6H$, and $H(CH_3C_6H_2F)_8H$. These compounds were all prepared from fluorobenzene or *p*-methylfluorobenzene as starting materials. Metalation of either of these starting compounds with *sec*-butyllithium in $(CH_2)_4O$ at -62 °C gave an ortho-lithiated product, which was oxidatively coupled with $Fe(acac)_3$ or $Cu(O_2CCF_3)_2$ in $(CH_2)_4O$ at 25 °C to give the corresponding two-unit products. Cross couplings of one- with two-unit oligomers gave three-unit oligomers. Couplings of two like two-unit oligomers gave four-unit oligomers, etc. Dilithiation of $H(C_6H_3F)_3H$ and carbonation of the product gave $HO_2C(C_6H_3F)_3CO_2H$, which was reduced $(BH_3{\cdot}(CH_2)_4O)$ to produce $HOCH_2(C_6H_3F)_3CH_2OH$. Treatment of this diol with $TsOCH_2CH_2OCH_2CH_2OTs$ in $(CH_2)_4O{\cdot}NaH$ gave the 36-membered cycle, $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$. Treatment of the diol with PBr_3 gave $BrCH_2(C_6H_3F)_3CH_2Br$, which with $HOCH_2CH_2OCH_2CH_2OH$ in $(CH_2)_4O{\cdot}NaH$ gave the 18-membered cycle, $(C_6H_3F)_3(CH_2OCH_2)_3$. The cavitands, $(CH_3C_6H_2F)_6$ and $(CH_3C_6H_2F)_8$, although they possess suitably sized cavities lined with unshared electron pairs, failed to bind any of the alkali metal ions, NH_4^+, $CH_3NH_3^+$, or t-$BuNH_3^+$ in $CDCl_3$. Cycles $(C_6H_3F)_3(CH_2OCH_2)_3$ and $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$ failed to extract detectable amounts of the picrate salts of the same cations into $CDCl_3$ from D_2O solutions. Although models show that $(CH_3C_6H_2F)_6$ is superbly organized for binding Li^+ or Na^+ ions, the electron pairs of the fluorine atoms appear totally unable to play such a role although its oxygen analogue, $(CH_3C_6H_2OCH_3)_6$, is a superb binder of these ions. The temperature dependence of the NMR spectra of $(CH_3C_6H_2F)_8$ shows that it undergoes ring inversion with an activation energy of 15.4 ± 0.3 kcal mol^{-1}.

Earlier papers have reported that whereas spherand **1** in $CDCl_3$ at 25 °C binds lithium and sodium picrates with >23 and 19 kcal mol^{-1} free energy, respectively, the noncyclic analogue **2** binds these salts with <6 kcal mol^{-1}.[2,3] The >13 kcal mol^{-1} difference between the spherand and its noncylic analogue **2** has been attributed to the fact that the spherand oxygens are organized for complexation during synthesis rather than during the complexing act (*principle of preorganization*). Nonspherand **2** is a mixture of hundreds of conformations, all but two of which must be frozen out to provide the octahedral arrangement of oxygens found in the spherand. Furthermore, unlike those of **1**, the unshared electron pairs of **2** are exposed to solvation, and desolvation costs must be paid for in terms of complexation free energies.



1, $(CH_3C_6H_2OCH_3)_6$



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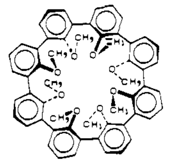

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Between these extremes of preorganization and the lack thereof lie cavitand **3**[4] and hemispherand **4**. In **3**, although each of the eight oxygens is anti to the two nearest oxygens to provide the arrangement of a square antiprism,[5] a crystal structure shows that four methyl groups turn inward and four outward to provide an ellipitcal cavity.[6] Thus the oxygens and four of the methyls of **3** are organized for binding large metal ions, but rotations of 180° about the other four Ar–OCH_3 bonds must occur to move the other four methyl groups if a cavity lined with electron pairs is to be available. A crystal structure of **4**[5] indicates the three methoxyl groups form a half-nest lined with unshared electron pairs. However, two inward-turned methylene groups of the chorand part of the compound fill the cavity, as is observed in the crystal structures of the chorands and cryptands.[5] These two hosts, being partially preorganized for binding, are generally stronger complexing agents than their chorand counterparts. Thus the degree of preorganization strongly influences the binding ability of hosts.

The present study addresses the question of whether precise preorganization for cooperative binding can compensate for the normal unavailability of the unshared electron pairs of covalently bonded fluorine to ligate metal ions.[7] Usually the oxygens of anisole are poor ligands, but spherand **1** is the strongest known binder of Li^+ and Na^+. Accordingly, syntheses of **5**, **6**, and **8** were undertaken, and their binding properties were examined.

Results and Discussion

Syntheses. The only type of reaction used in the syntheses of **5** and of **8–19** was the oxidative coupling of metalated fluorobenzenes or 4-methylfluorobenzenes.[8] Metalation of fluoro-

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(1) Support for the syntheses and complexation attempts by the Division of Basic Sciences of the Department of Energy (Contract AT(04-3), P.A. 218) is gratefully acknowledged by D. J. Cram, S. B. Brown, T. Taguchi, and M. Feigel. Support for the crystal structure work by the National Science Foundation is gratefully acknowledged by E. Maverick and K. N. Trueblood.

(2) Lein, G. M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 301–304.

(3) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6228–6232.

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(5) (a) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106. (b) Goldberg, I. *Cryst. Struct. Commun.* **1980**, *9*, 1201–1207.

(6) Trueblood, K. N.; Knobler, C. B., unpublished results.

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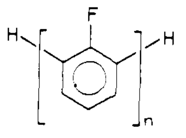
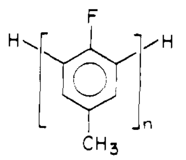


9, n = 2, $H(C_6H_3F)_2H$
10, n = 3, $H(C_6H_3F)_3H$
11, n = 4, $H(C_6H_3F)_4H$
12, n = 6, $H(C_6H_3F)_6H$
13, n = 8, $H(C_6H_3F)_8H$
14, n = 9, $H(C_6H_3F)_9H$

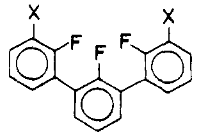


15, n = 2, $H(CH_3C_6H_2F)_2H$
16, n = 3, $H(CH_3C_6H_2F)_3H$
17, n = 4, $H(CH_3C_6H_2F)_4H$
18, n = 6, $H(CH_3C_6H_2F)_6H$
19, n = 8, $H(CH_3C_6H_2F)_8H$

benzene with *sec*-BuLi in $(CH_2)_4O$ at −62 °C gave material which was added to a solution of $Fe(acac)_3$ in $(CH_2)_4O$ at 25 °C to produce $H(C_6H_3F)_2H$ (**9**)[9] in 85% yield. Substitution of $Cu(acac)_2$, $Co(acac)_3$, or $CuCl_2$ for $Fe(acac)_3$ gave yields of 43%, 36%, and 31%, respectively. Substitution of 2-bromofluorobenzene (BuLi) for fluorobenzene in the original procedure gave 79% of **9**. In subsequent oxidative couplings, the polyfluoroaryls were directly metalated with *sec*-BuLi, and the organometallics were oxidized with $Fe(acac)_3$ unless otherwise indicated. The coupling of $H(C_6H_3F)_2H$ (**9**) with C_6H_5F and itself gave $H(C_6H_3F)_3H$ (**10**) and $H(C_6H_3F)_4H$ (**11**) in 36% and 27% yields, respectively. The coupling of $H(C_6H_3F)_2H$ with itself gave $H(C_6H_3F)_4H$ (**11**, 50%) and $H(C_6H_3F)_6H$ (**12**, 18%). Dimetalation of $H(C_6H_3F)_2H$ followed by oxidation gave mixtures of $H(C_6H_3F)_6H$ (**12**), $H(C_6H_3F)_8H$ (**13**), and cycles $(C_6H_3F)_6$ and $(C_6H_3F)_8$, whose components were not separated but which were detected by mass spectra. Similarly dimetalation of $H(C_6H_3F)_3H$ (**10**) and oxidation led to an unseparated mixture of $H(C_6H_3F)_6H$ (**12**), $H(C_6H_3F)_9H$ (**14**), and cycles $(C_6H_3F)_6$ and $(C_6H_3F)_9$, again detected only by mass spectra. Coupling of $H(C_6H_3F)_4H$ (**11**) gave $H(C_6H_3F)_8H$ (**13**, 24%). Coupling of $H(C_6H_3F)_3H$ with $Cu(OCOCF_3)_2$[10] substituted for $Fe(acac)_3$ in the procedure gave $H(C_6H_3F)_6H$ (**12**, 43%) and $H(C_6H_3F)_9H$ (**14**, 9%).

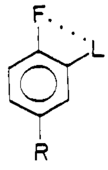
Since we failed in repeated attempts to isolate cycles $(C_6H_3F)_6$ and $(C_6H_3F)_8$ in a pure state because of their poor solubility properties, we turned to 4-methylfluorobenzene as our starting material. Metalation and coupling of 4-methylfluorobenzene gave $H(CH_3C_6H_2F)_2H$ (**15**, 89%), which was converted to $H(CH_3C_6H_2F)_4H$ (**17**) and $H(CH_3C_6H_2F)_6H$ (**18**) in 73% and 8% yields, respectively. Cross coupling of $CH_3C_6H_4F$ with $H(CH_3C_6H_2F)_2H$ (**15**) gave $H(CH_3C_6H_2F)_3H$ (**16**, 32%). Coupling of $H(CH_3C_6H_2F)_3H$ (**16**) with itself gave $H(CH_3C_6H_2F)_6H$ (**18**, 37%) plus a mixture of $H(CH_3C_6H_2F)_9H$ and cycle $(CH_3C_6H_2F)_6$ (**5**) characterized only by their mass spectra. Coupling of $H(CH_3C_6H_2F)_4H$ (**17**) with itself gave $H(CH_3C_6H_2F)_8H$ (**19**, 22%) plus a mixture of $H(CH_3C_6H_2F)_{12}H$ and cycle $(CH_3C_6H_2F)_8$ (**8**) characterized only by their mass spectra. Cyclization of $H(CH_3C_6H_2F)_6H$ (**18**) by dimetalation with *sec*-butyllithium and oxidation of the organometallic produced with $Cu(O_2CCF_3)_2$ gave $(CH_3C_6H_2F)_6$ (**5**, 10%). Similar cyclization of $H(CH_3C_6H_2F)_8H$ (**19**) gave $(CH_3C_6H_2F)_8$ (**8**, 9%).

The macrocycles $(C_6H_3F)_3(CH_2OCH_2)_3$ (**6**) and $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$ (**7**) were prepared as follows. Dimetalation of $H(C_6H_3F)_3H$ (**10**) with *sec*-butyllithium and treatment of the organometallic obtained with CO_2 gave $HO_2C(C_6H_3F)_3CO_2H$ (**20**, 74%), reduction of which with $BH_3{\cdot}(CH_2)_4O$ produced $HOCH_2(C_6H_3F)_3CH_2OH$ (**21**, 87%). Treatment of **21** with diethylene glycol ditosylate (NaH–$(CH_2)_4O$) gave only $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$ (**7**, 18% yield). Diol **21** was converted with PBr_3 to $BrCH_2(C_6H_3F)_3CH_2Br$ (**22**, 60%), which when cyclized with diethylene glycol (NaH–$(CH_2)_4O$) gave $(C_6H_3F)_3(CH_2OCH_2)_3$ (**6**, 53%).



20, X = CO_2H
21, X = CH_2OH
22, X = CH_2Br

The above syntheses utilize a new and efficient method for metalating fluoroaromatic compounds in positions ortho to the fluorines and converting these intermediates into substitution products. Previous syntheses of 2,2′-difluorobiphenyl and related compounds involved Ullman coupling of nitrobenzene derivatives, reduction of the nitro groups to amines, diazotization of the amines, and substitution of the nitrogen with fluorine.[9] A potential obstacle to our ortho metalation approach is the elimination of LiF from the organometallics to produce benzynes and their reaction products at temperatures greater than −50 °C.[11] Wittig et al.[12] converted *o*-lithiofluorobenzene at −70 °C to isolable silver or mercury derivatives, which when heated gave 2,2′-difluoro-1,1′-biphenyl in 77 and 82% yields, respectively.[12] Our syntheses demonstrate that $Fe(acac)_3$ oxidizes *o*-lithiofluoroaromatics to the putative radicals required for coupling *much faster* in $(CH_2)_4O$ at −62 °C than elimination to benzyne occurs. The carbonation of the *o*,*o*″-dilithio derivative of $H(C_6H_3F)_3H$ (**10**) at −62 °C to give $HO_2C(C_6H_3F)_3CO_2H$ (**20**) also shows these *o*-lithiofluoroaromatics to be useful synthetic intermediates for any reaction that occurs at or below this temperature.



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Structures of Cavitands. The crystal structure of macrocycle $(CH_3C_6H_2F)_6$ (**5**) indicates that the compound possesses symmetry $\bar{3}$ (approximately D_{3d}), with the fluorine atoms in an octahedral arrangement. Each molecule possesses a roughly cylindrical cavity with a diameter of ~1.5 Å and a depth of ~3.6 Å.

The crystal structures of $(CH_3C_6H_2OCH_3)_6$ (**1**)[13] and $(CH_3C_6H_2F)_6$ (**5**) provide interesting comparisons. The dihedral angle between the best planes of two attached aryls in **5** is 44°, considerably less than the 52° observed in **1**. Consequently, **5** is flatter than the $(CH_3C_6H_2O-)_6$ portion of **1**. The hole diameter of **1** is 1.62 Å, ~0.14 Å greater than that of **5**. The near-neighbor oxygen-to-oxygen distances in **1** are 2.92 Å, 0.29 Å longer than in **5**. The distance of each fluorine in **5** from the best plane of its attached aryl ring is 0.20 Å, the same as the distance in **1** for each oxygen from the best plane of its attached aryl ring. In both structures, the aryls are nonplanar, being folded about their CH_3–C_6H_2–X axes, in **5** by 5.7°, and in **1** by 6.3°. The overall deformations appear to be slightly greater in the oxygen- than in the fluorine-containing analogue.

The ^{19}F, ^{1}H, and ^{13}C NMR spectra of $(CH_3C_6H_2F)_6$ in $CDCl_3$ indicate that the compound possesses the D_{3d} symmetry of structure **5** in solution as well as in its crystalline form. One set of signals is observed for the six equivalent aromatic rings (see Table I). The ^{19}F NMR spectrum consists of one singlet, and the ^{1}H and ^{13}C NMR spectra show the 2- and 6-positions and the 3- and 5-positions of each benzene ring to be equivalent in

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[8] This reaction was invented for the express purpose of synthesizing the spherands based on anisole units: Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752–6754.

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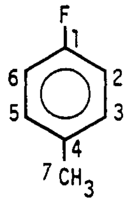
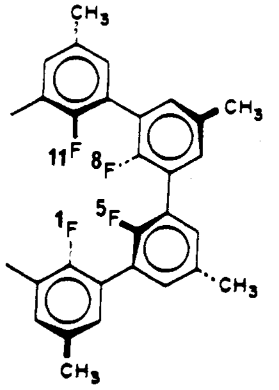
Table I. Chemical Shifts (δ) in NMR Spectra (ppm) of $(CH_3C_6H_2F)_6$ (5) and $(CH_3C_6H_2F)_8$ (8) in $CDCl_3$, ^{19}F Relative to $CFCl_3$, ^1H and ^{13}C Relative to $(CH_3)_4Si$[a]



compd	T, K	δ (^{19}F)	δ, ^1H position 3, 5	7
5	298	112.8	7.25	2.44
8	330	vb[b]	7.17[c]	2.39
8	258	117.0	7.19[d]	2.40
		116.1	7.14[d]	2.35

[a] ^{13}C for 5 at 298 K: δ 155.5 (C-1, $^1J_{CF}$ = 269 ± 4 Hz), 122.6 (C-2,6), 129.0 (C-3,5), 132.5 (C-4), 19.9 (C-7). [b] Very broad. [c] $^4J_{HF}$ = 4.9 Hz. [d] $^4J_{HF}$ = 5.8 Hz.

accordance with the vertical symmetry planes that divide each benzene ring. A $^5J_{FF}$ coupling between each set of fluorine near-neighbors of 39.3 Hz is observed in the ^{13}C satellite of the ^{19}F spectrum. The magnitude of $^5J_{FF}$ indicates the presence of "through-space" coupling, which requires close proximity of the fluorine atoms. From the theoretical dependence of $^5J_{FF}$ on the dihedral angle of the two C=C planes in 1,4-difluorobutadienes,[14] we estimate the dihedral angle between the planes of attached benzene rings to be 36°, which is somewhat different from the 44° observed in the crystal structure.



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The multiplet of the ^{13}C satellites in 5 could only be reproduced by simulation if the coupling constants between fluorines, which are non-neighbors, have substantial values: $^8J_{FF}$ = 6.1 ± 2 Hz, $^{11}J_{FF}$ = −3.8 ± 3.5 Hz. The error limits were estimated to be five times the standard deviation given by the iteration program (see Experimental Section) to account for the low signal-to-noise ratio in the weak and complicated multiplets of the ^{13}C satellites. Even with these high error limits, we think that at least $^8J_{FF}$ is established. These long-range couplings suggest the possibility that this unique arrangement of six fluorines provides a cyclic, six-fluorine bonding system!

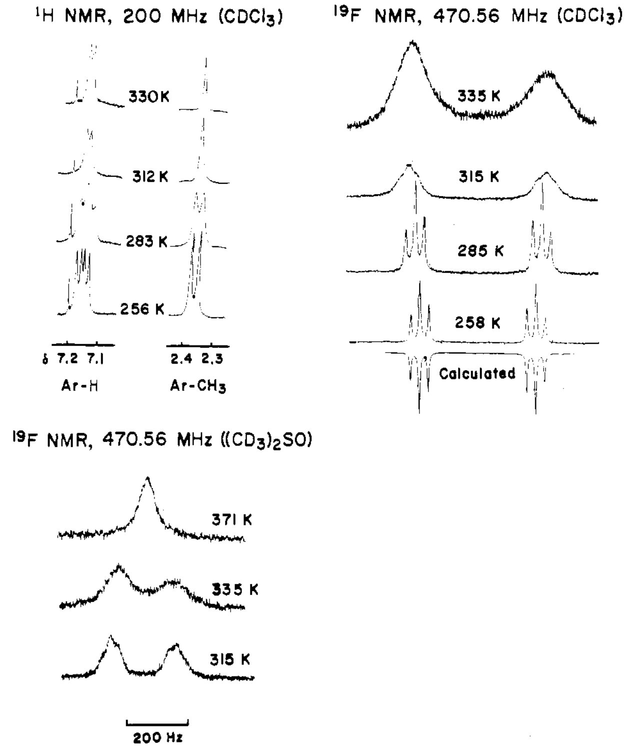

Figure 1. NMR spectra of **8b** as temperature is changed.

Unfortunately, crystals of $(CH_3C_6H_2F)_8$ suitable for crystal structure determination have not been successfully prepared. The NMR spectra of this cavitand in $CDCl_3$ provided interesting structural information. The ^1H and ^{19}F NMR spectra exhibit broad lines at ambient and higher temperatures. The signals sharpen as the solution is cooled. At 258 K the observed pattern is consistent with two types of aromatic rings within the same molecule. The 2- and 6-positions of each benzene ring are equivalent, as are the 3- and 5-positions. The fluorine coupling with each of its two near fluorine neighbors is directly observed in the ^{19}F NMR spectrum to give a pattern of two virtual triplets with a coupling constant of $^5J_{FF}$ 32.5 Hz (Figure 1). The dihedral angle between the two bound phenyl rings is estimated with this value to be about 40°.

Molecular models (CPK) of three apparently strain-free conformations of $(CH_3C_6H_2F)_8$ can be assembled. Conformation **8a** belongs to the point group D_{4d} and has a symmetry number of eight, and all eight aryls and their substituents are in equivalent magnetic environments. Conformation **8b** belongs to the point group D_{2d}, has a symmetry number of 4, and possesses two kinds of aryls. Four alternate aryls are nearly coplanar, two aryls opposite one another place their fluorines on one side of that plane, and the two remaining opposite aryls place their fluorines on the other side. Conformation **8c** belongs to the point group C_s, has a symmetry number of 1, and possesses five different kinds of aryl groups.

The 258 K NMR spectra of $(CH_3C_6H_2F)_8$ indicate that only conformation **8b** is populated, since two different kinds of fluorines are present. At higher temperatures, the NMR signals broaden and coalesce, and sharp, averaged lines are observed above 330 K in the ^1H, and above 370 K in the ^{19}F spectra. Clearly, ring inversions interconvert the two types of aryls of **8b**. The activation energy barrier in $CDCl_3$ is estimated at 315 K to be $\Delta G^{\ddagger}$ = 15.4 ± 0.3 kcal mol^{-1} from line broadening of the ^{19}F NMR spectra. The two exchange-broadened resonances have different line widths at temperatures between 300 and 340 K in $CDCl_3$ (see Figure 1), CD_2Cl_2, $(CD_3)_2CO$, $C_2D_2Cl_4$, and $(CD_3)_2SO$. This effect may be due to different temperature-dependent transverse relaxation times, to an exchange mechanism involving nonsymmetrical permutations of transitions, or to an equilibration with small amounts of a second conformation that is not populated at the low temperature. At present, these possibilities cannot be distinguished.

The interesting question arises as to why conformation **8b** should be the most stable of the three. On the basis of symmetry properties alone at 300 K, **8c** should be 1.2 kcal mol^{-1} more stable than **8a**, and more stable than **8b** by 0.8 kcal mol^{-1}. Other effects appear to dominate. Estimations of the cavity volumes of the three conformations made from CPK molecular model measurements with each of the fluorines contacting its two neighbors provide the following relative values: **8b** normalized to 1; **8c**, 1.3; **8a**, 1.6.

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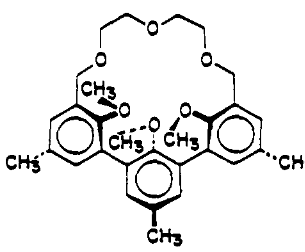
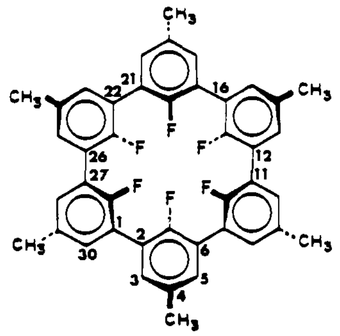
(14) Hiras, K.; Nakatsuji, H.; Kato, H. J. Am. Chem. Soc. 1973, 95, 31-41.

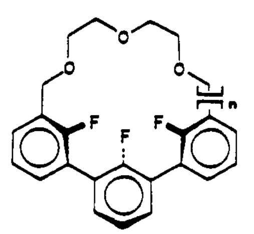
Chart I



4, $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$

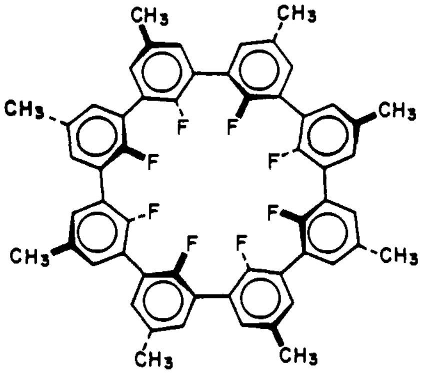


5, $(CH_3C_6H_2F)_6$

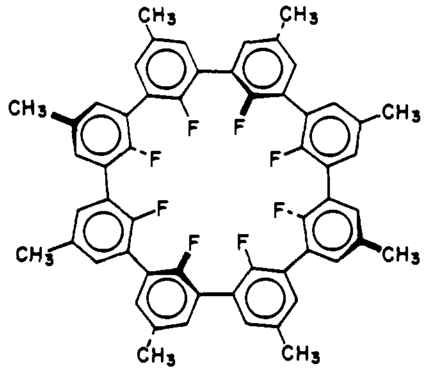


6, $(C_6H_3F)_3(CH_2OCH_2)_3$, n = 1

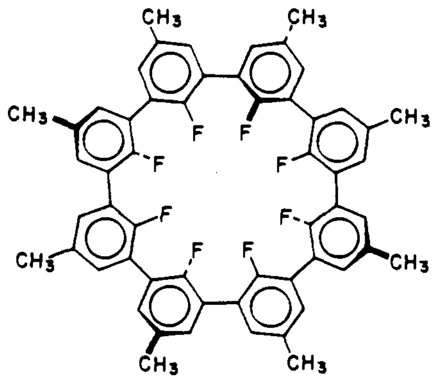
7, $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$, n = 2



8a, $(CH_3C_6H_2F)_8$



8b, $(CH_3C_6H_2F)_8$



8c, $(CH_3C_6H_2F)_8$

Although inexact, these values indicate that **8b** has by far the smallest cavity, **8c** is next, and **8a** has the largest. We suggest that along with other effects that determine the relative thermodynamic stabilities of conformers, there is one which tends to minimize the volume of enforced cavities, and that it might, at low temperature, control the conformation of $(CH_3C_6H_2F)_8$. The effect is undoubtedly small, and is caused by the same factors that tend to eliminate cavities in crystals.

Nonbonding Properties of $(CH_3C_6H_2F)_6$ (5), $(C_6H_3F)_3(CH_2OCH_2)_3$ (6), $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$ (7), and $(CH_3C_6H_2F)_8$ (8). The ^{19}F NMR spectra of 0.0031 M solutions of $(CH_3C_6H_2F)_6$ (**5**) in $CDCl_3$ were the same in the presence and absence of an equimolar quantity of the ClO_4^- salts of Li^+, Na^+, K^+, Rb^+, or Cs^+. The ^1H NMR spectra in 2% $(CD_3)_2SO$ in $CDCl_3$ of $(CH_3C_6H_2F)_6$ solutions were identical in the presence and absence of equimolar concentrations of each of the same salts. This behavior contrasts with that of $(CH_3C_6H_5OCH_3)_6$ (**1**), whose $ArCH_3$ and ArH protons underwent marked and easily detected changes in chemical shifts due to complexation when $LiClO_4$ or $NaClO_4$ was present.[3] We conclude that $(CH_3C_6H_2F)_6$ does not complex these ions.

Solutions of macrocycles $(C_6H_3F)_3(CH_2OCH_2)_3$ (**6**) or $[(C_6H_3F)_3(CH_2OCH_2)_3]_2$ (**7**) at 0.015 M concentration in $CDCl_3$ failed to extract from D_2O detectable amounts of dissolved picrate salts of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and $(CH_3)_3CNH_3^+$ at 0.010 to 0.015 M concentrations. Thus these cycles show binding free energies ($-\Delta G^\circ$ values) well below the 6 kcal mol^{-1} threshold value detectable by this method.[15]

The inability of $(CH_3C_6H_2F)_6$ or $(C_6H_3F)_3(CH_2OCH_2)_3$ to bind cations is in marked contrast to the behavior of their analogues, $(CH_3C_6H_2OCH_3)_6$ (**1**) and $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$ (**4**). In $CDCl_3$ at 25 °C, $(CH_3C_6H_2OCH_3)_6$ binds the picrate salts of Li^+ with a $-\Delta G°$ value of >23, and Na^+ with a value of 19 kcal mol^{-1},[2] whereas under the same conditions the similarly organized $(CH_3C_6H_2F)_6$ shows no detectable binding. In $CDCl_3$ at 25 °C, $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$ binds the eight cations with $-\Delta G°$ values that range from 7 to 12 kcal mol^{-1},[16] whereas the similarly organized $(CH_3C_6H_2F)_3(CH_2OCH_2)_3$ shows <6 kcal mol^{-1} binding free energy.

The ring inversion that **8b** undergoes at higher temperatures provided a possible means of detecting host-guest complexation effects of low magnitude in which macrocycle $(CH_3C_6H_2F)_8$ might serve as the host and solvent as the guest. The ring inversion pathway involving the least structural change is as follows: **8b** → **8c** → **8a** → **8c′** → **8b′**, etc. We visualized the possibility that solvent-host complexation might affect the relative stabilities of the complexes of **8b**, **8c**, and **8a** differently as the character of the guest (solvent) was changed, and thus the activation free energies for ring inversion might change with changes in solvent. A line-width analysis of the ^{19}F NMR spectra of $(CH_3C_6H_2F)_8$ in a variety of solvents at 315 K provided the following $\Delta G^{\ddagger}$ values (±0.3 kcal mol^{-1}) for activation free energy barriers to ring inversion: CD_2Cl_2, 15.7; $(CD_3)_2SO$, 15.5; $CDCl_3$, 15.4; $(CD_3)_2CO$, 15.3; $C_2D_2Cl_4$, 15.1. The solvent dependence of the activation energy is less than 1 kcal mol^{-1}, which is in the range expected for biphenyl rotation. At 258 K, in the four solvents that are liquid at that temperature ($(CD_3)_2SO$ is not), only the spectrum of **8b** was visible. Thus within experimental error, the complexation that exists between solvents and any of the conformers of **8** changes neither the relative stabilities of the conformers nor the activation energies for their interconversion.

We conclude that although superb preorganization of ligating sites can vastly enhance the poor intrinsic binding ability of $ArOCH_3$ groups, the intrinsic ability of the fluorines of ArF groups to ligate appears too low to be brought on scale by their being organized to act cooperatively. The question arises whether the fluorines of ArF can ever act as ligating sites. Possibly they play that role in the *o*-fluoroaryllithium compounds (**23** is prototypical) that are the key intermediates in our syntheses of compounds **5**–**19**.

Experimental Section

General. Melting points (uncorrected) were measured on a Thomas-Hoover apparatus from 20 to 250 °C and on a Mel-Temp metal block for the range 250–360 °C. Unless otherwise specified, the ^1H and ^{13}C NMR spectra were taken on a Bruker WP-200 spectrometer with δ values given in ppm from tetramethylsilane. The ^{19}F NMR spectra were taken on a JEOL-FX 90-Q spectrometer at 84.25 MHz without proton decoupling with $CFCl_3$ as an internal standard and on a Bruker WM-500 spectrometer at 470.56 MHz with proton decoupling without a standard. Mass spectra were recorded on an AE-1 Model MS-9 double-focusing spectrometer interfaced by Kratos Co. to a Data General Nova 3. All elemental analyses were within 0.30% of theory. All chemicals were reagent grade. All reactions were conducted under an atmosphere of dry nitrogen or argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone ketyl prior to use. Benzene and dimethylformamide (DMF) were distilled from 4-Å molecular sieves and stored over them. Dichloromethane was carefully distilled. Bromine was stored over P_2O_5. All reactions were run in equipment flame-dried under N_2 or Ar. Solutions of *sec*-butyllithium in cyclohexane were obtained from Alfa-Ventron and were titrated to a 1,10-phenanthroline end point before use. Reported R_f values were obtained on thin layer plates of silica gel 60 (E. M. Merck, layer thickness 0.25 mm).

2,2′-Difluoro-1,1′-biphenyl (9). Procedure A. To a stirred solution of 19.35 g (0.201 mol) of fluorobenzene in 300 mL of THF held at −62 °C under Ar was added dropwise 148 mL of a 1.49 M solution (0.22 mol) of *sec*-butyllithium in cyclohexane. The resulting solution (light yellow) was stirred for 3 h at −62 °C and then cannulated cold into a solution of 85 g (0.24 mol) of $Fe(acac)_3$ (dry) in 900 mL of THF stirred under Ar at ambient temperature. After stirring for 1 h, the resulting mixture was poured into 1.5 L of H_2O and 200 mL of concentrated hydrochloric acid. The mixture was extracted with Et_2O (four 250-mL portions), the combined extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. High vacuum film drying of the mobile oil residue removed the 2,4-pentanedione present. The remaining crystalline mass, dissolved in CH_2Cl_2, was submitted to flash chromatography on silica gel (30 × 3.5 cm column). The product (**9**) eluted in the first 800 mL of CH_2Cl_2 gave R_f 0.77 in CH_2Cl_2. Evaporation of solvent gave crude material, which when recrystallized from absolute EtOH gave 16.2 g (85%) of **9** as white plates: mp 116–118 °C (lit. 117–117.5 °C);[9] ^{19}F NMR ($CDCl_3$) δ −115.29. Anal. C, H.

Application of procedure A to experiments that involved butyllithium as metalating agent and $Co(acac)_3$ in THF, $Cu(acac)_2$ in pyridine, or $CuCl_2$ (added as a solid to the THF solution of the organometallic) gave reduced yields of product.

2,2′-Difluoro-5,5′-dimethyl-1,1′-biphenyl (15). Application of procedure A to 2.32 g (0.021 mol) of 4-methylfluorobenzene, 8.91 g (0.025 mol) of $Fe(acac)_3$, and 16.1 mL of a 1.31 M solution of *s*-BuLi in cyclohexane (0.021 mol) in a total of 300 mL of THF gave a product purified by flash chromatography and distillation to give **15** as a colorless oil: R_f 0.74 (CH_2Cl_2); 2.03 g (89%); ^{19}F NMR ($CDCl_3$) δ −120.75; ^1H NMR ($CDCl_3$) δ 2.35 (s, CH_3, 6); anal., C and H.

2,2′,2″-Trifluoro-1,1′:3′,1″-terphenyl (10) and 2,2′,2″,2‴-Tetrafluoro-1,1′:3′,1″:3″,1‴-quaterphenyl (11). Procedure A was applied to 3.81 g (0.020 mol) of $H(C_6H_3F)_2H$ (**9**) mixed with 3.89 g (0.040 mol) of fluorobenzene in 250 mL of THF, 44 mL of 1.31 M *s*-BuLi (0.060 mol) in cyclohexane, and 22.7 g (0.064 mol) of $Fe(acac)_3$ in 500 mL of THF. The product after flash chromatography was submitted to careful chromatography on silica gel (30 × 3.5 cm column) in hexane to give the following fractions characterized by TLC in hexane: A, 250 mL, forerun; B, 750 mL, R_f 0.24, **9**, 2.185 g, 29% crude and 22% recrystallized yield; C, 200 mL, R_f 0.22 and 0.09, 0.17 g; D, 1650 mL, R_f 0.12, **10**, 2.966 g, 39% crude, 2.17 g, 29% after recrystallization from 95% EtOH, [mp 72–74 °C; ^{19}F NMR ($CDCl_3$) δ −115.07 (F, 2), −116.98 (F, 1). Anal. C, H]; E, 650 mL, R_f 0.10 and 0.05, 0.022 g; F, 5400 mL, R_f 0.05, **11**, 1.172 g (14%), 1.08 g after recrystallization from absolute EtOH [mp 147–148 °C, ^{19}F NMR ($CDCl_3$) δ −115.07 (F, 2), −116.70 (F, 2). Anal. C, H]. Compound $H(C_6H_3F)_4H$ (**11**) was also produced by procedure A from $H(C_6H_3F)_2H$ (**9**) as the only starting material, 70% yield, mp 147–148 °C.

2,2′,2″-Trifluoro-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl (16). Application of procedure A to 4.93 g (0.045 mol) of 4-methylfluorobenzene, 3.25 g (0.0149 mol) of 2,2′-difluoro-5,5′-dimethyl-1,1′-biphenyl (**15**) in 200 mL of THF, 46 mL of *sec*-BuLi (1.3 M, 0.0598 mol in cyclohexane), and 21.1 g (0.0597 mol) of $Fe(acac)_3$ in 500 mL of THF gave a crude product which after flash chromatography was carefully chromatographed on a 39 × 4.5 cm column of silica gel in hexane. The following fractions were characterized by TLC in hexane: A, 1500 mL, 0.066 g, R_f 0.42; B, 3000 mL, 2.064 g (25%), R_f 0.22, recovered **15**; C, 2000 mL, 0.078 g, R_f 0.18, 0.10; D, 9500 mL, 2.571 g (32%), R_f 0.08, **16**, viscous oil purified by molecular distillation (160 °C at 6 × 10^{-5} mm) [^{19}F NMR ($CDCl_3$) δ −120.43 (F, 2), −122.25 (F, 2); ^1H NMR ($CDCl_3$) δ 2.356 (s, 6, CH_3), 2.40 (s, 3, CH_3). Anal. C, H].

2,2′,2″,2‴-Tetrafluoro-1,1′:3′,1″:3″,1‴-quaterphenyl (11) and 2,2′,2″,2‴,2⁗,2′′′′′-Hexafluoro-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′-sexiphenyl (12). Application of procedure A to 4.61 g (0.0243 mol) of $H(C_6H_3F)_2H$ (**9**) in 200 mL of THF, 20 mL of *sec*-BuLi in cyclohexane (1.5 M, 0.030 mol), and 13.30 g (0.038 mol) of $Fe(acac)_3$ in 450 mL of THF gave after flash chromatography a crude product carefully chromatographed on a 30 × 4.5 cm column of silica gel with 30:1 (v/v) hexane–CH_2Cl_2. Compound **11** was eluted with 10:1 (v/v) hexane–CH_2Cl_2 to give after recrystallization from absolute ethanol 2.313 g (50%), mp 148–149 °C. Compound **12** was eluted with 5:1 (v/v) hexane–CH_2Cl_2 to give, after recrystallization from cyclohexane–benzene: 0.809 g (18%), mp 180–182 °C; ^{19}F NMR ($CDCl_3$–$(CD_3)_2SO$) δ −115.61 (F, 2), −117.11 (F, 4), (C_5D_5N–$(CD_3)_2SO$, 3:1 (v/v) δ −114.22 (F, 2), −115.84 (F, 4)); MS, M^+ 566 (100); anal., C, H, F.

2,2′,2″,2‴,2⁗,2′′′′′-Hexafluoro-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′-sexiphenyl (12) and 2,2′,2″,2‴,2⁗,2′′′′′,2′′′′′′,2′′′′′′′,2′′′′′′′′-Nonafluoro-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′:3′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′:3′′′′′′′,1′′′′′′′′-nonaphenyl (13). Application of procedure A to $(C_6H_3F_3)_3$ (**10**), 2.843 g (0.010 mol) in 70 mL of THF, 7.5 mL of *s*-BuLi solution in cyclohexane (1.47 M, 0.11 mol), and 5.424 g (0.015 mol) of dry $Cu(O_2CCF_3)_2$[10] in 250 mL of THF gave Et_2O extracts that were washed with four 40-mL portions of 10% NH_3 in water to remove the copper ion. The product mixture was carefully chromatographed on silica gel. The fraction that eluted with hexane–CH_2Cl_2, 5:1 (v/v), gave 0.803 g (28%) of **10**, mp 73–75 °C. The fractions eluted with hexane–CH_2Cl_2, 3:1 (v/v)

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[15] Koenig, K. E.; Lein, G. M.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553–3566.

[16] Cram, D. J.; Dicker, I. B.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6828–6830.

gave first **12**, 1.223 g (43%) after recrystallization from cyclohexane–benzene, mp 180–182 °C, and then **13**, 0.245 g (9%) after recrystallization from benzene, mp 203–204.5 °C; ^{19}F NMR ($CDCl_3$–C_5D_5N, 1:1, v/v) δ −114.04 (F, 2), −115.55 (F, 7). Anal. C, H, F.

2,2′,2″,2‴,2⁗,2′′′′′,2′′′′′′,2′′′′′′′-Octafluoro-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′:3′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′-octaphenyl (13). Application of procedure A to 8.039 g (0.0212 mol) of $H(C_6H_3F)_4H$ (**11**) in 200 mL of THF, 15 mL of *sec*-BuLi (1.45 M in cyclohexane, 0.021 mol), and 9.0 g (0.0255 mol) of $Fe(acac)_3$ in 400 mL of THF gave a product which was carefully chromatographed on silica gel. The fraction eluted with hexane–CH_2Cl_2 (8:1, v/v) gave 1.82 g (23%) of **11**, mp 147–148 °C. The fraction eluted with hexane–CH_2Cl_2 (4:1, v/v) gave **13**, which was recrystallized from cyclohexane–benzene to give 1.856 g (24%), mp 210.5–212 °C; ^{19}F NMR ($CDCl_3$–$(CD_3)_2SO$) δ −115.78 (F, 2), −117.29 (F, 6); MS, M^+ 754 (100). Anal. C, H. F.

2,2′,2″,2‴-Tetrafluoro-5,5′,5″,5‴-tetramethyl-1,1′:3′,1″:3″,1‴-quaterphenyl (17) and 2,2′,2″,2‴,2⁗,2′′′′′-Hexafluoro-5,5′,5″,5‴,5⁗,5′′′′′-hexamethyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′-sexiphenyl (18). Application of procedure A to $H(CH_3C_6H_2F)_2H$ (**15**), 8.72 (0.040 mol) in 200 mL of THF, 28 mL of *sec*-BuLi in cyclohexane (1.45 M, 0.040 mol), and 15.50 g (0.044 mol) of $Fe(acac)_3$ in 300 mL of THF gave a product that was flash chromatographed and then carefully chromatographed on a 33 × 4.5 cm silica gel column at medium pressure. The fraction eluted with hexane–CH_2Cl_2 (50:1, v/v) gave 6.379 g (73%) of **17** as a glass; ^{19}F NMR ($CDCl_3$) δ −120.53 (F, 2), −122.15 (F, 2); ^{1}H NMR ($CDCl_3$) δ 2.344 (s, 6, CH_3), 2.393 (s, 6, CH_3); MS, M^+ 434, (100). Anal. C, H. F. The fraction eluted with hexane–CH_2Cl_2 (10:1, v/v) gave 0.671 g (8%) of **18** (see alternate synthesis and characterization below).

2,2′,2″,2‴,2⁗,2′′′′′-Hexafluoro-5,5′,5″,5‴,5⁗,5′′′′′-hexamethyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′-sexiphenyl (18). Application of procedure A to 1.939 g (0.00594 mol) of $H(CH_3C_6H_2F)_3H$ (**16**) in 80 mL of THF, 4.1 mL of *sec*-BuLi in cyclohexane (1.45 M, 0.006 mol), and 3.17 g (0.009 mol) of $Fe(acac)_3$ in 150 mL of THF gave a product that was carefully chromatographed on a 25 × 4.5 cm column of silica gel in hexane–CH_2Cl_2 (8:1, v/v). The same solvent eluted first starting material **16** (0.390 g, 20%), and then 0.727 g (37%) of **18** as a colorless glass: ^{19}F NMR ($CDCl_3$) δ −120.54 (F, 2), −122.15 (F, 4); ^{1}H NMR ($CDCl_3$) δ 2.348 (s, 6, CH_3), 2.393 (s, 12, CH_3); MS, M^+ 650 (100). Anal. C, H. F. Further elution of the column gave 0.134 g of a white powder, whose mass spectrum gave *m/e* 974 (100), 975 (71), 976 (21).

2,2′,2″,2‴,2⁗,2′′′′′,2′′′′′′,2′′′′′′′-Octafluoro-5,5′,5″,5‴,5⁗,5′′′′′,5′′′′′′,5′′′′′′′-octamethyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗,1′′′′′:3′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′-octaphenyl (19). Application of procedure A to 5.23 g (0.012 mol) of $H(CH_3C_6H_2F)_4H$ (**17**) in 100 mL of THF, 8.3 mL of *sec*-BuLi in cyclohexane (1.45 M, 0.012 mol), and 5.297 g (0.015 mol) of $Fe(acac)_3$ in 300 mL of THF gave material that was carefully chromatographed on silica gel. Hexane–CH_2Cl_2 (20:1, v/v) eluted 1.223 g (23%) of **17**, and hexane–CH_2Cl_2 (5:1, v/v) eluted 1.128 g (22%) of **19**, a colorless glass: ^{19}F NMR ($CDCl_3$) δ −122.151 (F, 6), −120.645 (F, 2); ^{1}H NMR ($CDCl_3$) δ 2.347 (s, 6, CH_3), 2.390 (s, 18, CH_3); MS, M^+ 866 (100). Anal. C, H, F. Elution of the column with hexane–CH_2Cl_2 (2:1, v/v) gave 0.589 g (11%) of a mixture of 10:1 $H(CH_3C_6H_2F)_{12}H$ and $(CH_3C_6H_2F)_8$ (**8**), as shown by mass spectra, ^{19}F NMR, and TLC analysis. The $H(CH_3C_6H_2F)_{12}H$ in $CDCl_3$ gave ^{19}F NMR δ −120.59 (F, 2), −122.15 (F, 10).

31,32,33,34,35,36-Hexafluoro-4,9,14,19,24,29-hexamethylheptacyclo[25.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}.1^{22,26}]hexatriconta-1(31),2,4,6(36),7,9,11(35),12,14,16(34),17,19,21(33),22,24,26(32),27,29-octadecaene (5). Procedure A was applied to 0.697 g (1.07 mmol) of $H(CH_3C_6H_2F)_6H$ (**18**) in 30 mL of THF, 2.8 mL of *sec*-BuLi in cyclohexane (1.45 M, 4 mmol), and 2.17 g (6 mmol) of $Cu(O_2CCF_3)_1$^{10} (dried at 120 °C at 0.1 mm) in 500 mL of THF. The reaction mixture was stirred for 16 h at 25 °C, and then shaken with 100 mL of 10% NH_4OH solution in water. The aqueous layer was washed with 200 mL of Et_2O, and the combined organic phases were washed four times with 30-mL portions of 10% NH_4OH in water and with 20 mL of brine. The combined water layers were extracted again with 200 mL of Et_2O, and this ether layer was washed with two 20-mL portions of 10% NH_4OH in water and 20 mL of brine. The combined organic extracts were concentrated under reduced pressure, the residue dissolved in 50 mL of THF, was added to 30 g of silica gel, and the solvent was evaporated to dryness under vacuum. The solid was loaded on top of a 20 × 3 cm silica gel column in hexane, and **5** was eluted with hexane–CH_2Cl_2 (4:1, v/v) to give crude product. This material was dissolved in 5 mL of THF and precipitated with 10 mL of hexane to give 0.064 g of **5**, R_f 0.32 (cyclohexane–CH_2Cl_2, 3:1, v/v). This material was sublimed at 310–320 °C at 10^{-5} torr, and the sublimate was crystallized from THF to give 0.050 g (8.6%) of **5**, mp >360 °C; ^{19}F NMR ($CDCl_3$) δ −112.883 (s); ^{1}H NMR ($CDCl_3$) δ 2.443 (s, 18, CH_3), 7.257 (s, 12, ArH); ^{13}C NMR ($CDCl_3$) δ 20.875 (C-7), 123.70 (C-1 and C-3), 129.765 (C-4 and C-6), 132.962 (C-5); MS, 648 (M^+, 100), 649 (M^+ + 1, 43), 650 (M^+ + 2, 10), 324 (M^{2+}, 13); high-resolution MS, calcd for $C_{42}H_{30}F_6$ 648.2252; found 648.2278 (highest mass peak and highest intensity). Anal. C, H, F.

41,42,43,44,45,46,47,48-Octafluoro-4,9,14,19,24,29,34,39-octamethylnonacyclo[35.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}.1^{22,26}.1^{27,31}.1^{32,36}]octaquaterconta-1(41),2,4,6(48),7,9,11(47),12,14,16(46),17,19,21(45),22,24,26(44),27,29,31(43),32,34,36(42),37,38-tetracosaene (8). Application of procedure A to 1.220 g (2.8 mmol) of $H(CH_3C_6H_2F)_4H$ (**17**) in 100 mL of THF, 9 mL of *sec*-BuLi in cyclohexane (1.44 M, 13 mmol), and 5.30 g (15 mmol) of $Fe(acac)_3$ in 1 L of THF gave a final reaction mixture that was stirred for 16 h at 25 °C. The mixture was evaporated under reduced pressure to 100 mL and was combined with a second 100-mL mixture obtained identically with the first except that 1.215 g (2.8 mmol) of **17** was used. This mixture was shaken with 200 mL of 3 N hydrochloric acid, 500 mL of benzene, and 100 mL of Et_2O. The aqueous layer was extracted with a mixture of 500 mL of benzene and 100 mL of Et_2O, and the combined extracts were washed successively with three 40-mL portions of 3 N hydrochloric acid and one 100-mL portion of water. The organic layer was dried ($MgSO_4$) and evaporated. The residue was chromatographed four times on silica gel with a cyclohexane–benzene (3:1, v/v) elution to give 0.263 g of a white powder homogeneous to TLC (R_f 0.11, cyclohexane–benzene, 3:1, v/v). This material was recrystallized from CCl_4, and the residues were recrystallized from THF–hexane to give 0.139 g (8.6%) of **8**, mp 188–191 °C; ^{19}F NMR ($CDCl_3$) δ −116.577 (m); ^{1}H NMR ($CDCl_3$) δ 2.389 (s, 24, CH_3), 7.255 (m, 16, ArH); ^{13}C NMR ($CDCl_3$) δ 20.684 (s, C-7), 124.294 (d, C-1, C-3), 131.282 (s, C-4, C-6), 133.178 (s, C-5), 155.63 (d, C-1, $J_{C\text{-}1\text{-}F}$ 103 Hz); MS, 864 (M^+, 100), 865 (M^++1, 59), 866 (M^++2, 17), 432 (M^{2+}, 34). Anal. C, H, F.

2,2′,2″-Trifluoro-1,1′:3′,1″-terphenyl-3,3″-dicarboxylic Acid (20). Compound $H(C_6H_3F)_3H$ (**10**), 1.42 g (0.005 mol) in 250 mL of THF, was dilithiated with 15.4 mL of *sec*-BuLi in cyclohexane (1.3 M, 0.020 mol) as in procedure A at −62 °C. The reaction mixture was stirred for 4 h at −62 °C, and then CO_2 gas was vigorously bubbled through the reaction mixture for 15 min during which the temperature rose to −44 °C. The reaction flask was removed from the cooling bath and allowed to come to ambient temperature while CO_2 was bubbling through it (15 min). The mixture was shaken with 150 mL of water and 20 mL of concentrated hydrochloric acid. The aqueous layer was saturated with $MgSO_4$ and vigorously extracted with wet THF three times. The combined THF solutions were evaporated under reduced pressure to give a mixture of a white solid and water which was filtered. The white solid was recrystallized from 95% EtOH to give 1.38 g (74%) of diacid **20**, mp 324–328 °C; ^{19}F NMR ($(CD_3)_2SO$) δ −112.62 (F, 2), −116.12 (F, 1). Anal. C, H.

2,2′,2″-Trifluoro-1,1′:3′,1″-terphenyl-3,3″-dimethanol (21). To a solution stirred under Ar of 0.372 g (0.001 mol) of diacid **20** in 55 mL of THF was added 3.3 mL of $BH_3{\cdot}THF$ (1 M, 0.0033 mol) via syringe. The solution was stirred at ambient temperature for 3 h and at reflux for 3 h. The turbid mixture was treated dropwise with 10 mL of H_2O followed by 20 mL of water saturated with K_2CO_3. The aqueous layer was extracted with three 40-mL portions of Et_2O, and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under vacuum to give 0.388 g of white solid. This diol was recrystallized from $CHCl_3$–hexane to give 0.300 g (87%) of **21**, mp 133–134 °C; R_f (Et_2O) 0.26; ^{19}F NMR (6:1, $CDCl_3$:$CD_3)_2SO$, v/v) δ −116.6 (F, 1), −122.09 (F, 2); ^{1}H NMR ($CDCl_3$) δ 1.81 (t, 2, *J* 6 Hz, OH), 4.83 (d, 4, *J* 6 Hz, CH_2). Anal. C, H.

3,3″-Bis(bromomethyl)-2,2′,2″-trifluoro-1,1′:3′,1″-terphenyl (22). Diol **21** (1.37 g, 3.97 mmol) was suspended in 85 mL of benzene, and 2.16 g (8 mmol) of PBr_3 was added. The mixture was stirred for 14 h at 25 °C under dry conditions and then shaken with 20 mL of H_2O saturated with $NaHCO_3$ and 40 mL of brine. The aqueous layer was washed with three successive 50-mL portions of $CHCl_3$, the combined organic solutions were washed with brine and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2–hexane to give **22**, 1.13 g (60%), mp 171–172 °C; R_f 0.79 (CH_2Cl_2); ^{19}F NMR (10:1, $CDCl_3$:$(CD_3)_2SO$, v/v) δ −166.60 (f, 1); −122.02 (F, 2); ^{1}H NMR ($CDCl_3$) δ 4.587 (s, 4 H). Anal. C, H.

25,26,27-Trifluoro-13,16,19-trioxatetracyclo[19.3.1.1^{2,6}.1^{7,11}]pentacosa-(25),2,4,6(27),7,9,11(26),21,23-nonaene (6). Procedure B. A mixture of 120 mg of 50% NaH (weighed, then washed five times with dry pentane, 2.5 mmol) and 100 mL of THF was stirred under reflux, and over a 12-h period a 25-mL THF solution of dibromide **22** (0.330 g, 0.7 mmol) and dry diethylene glycol (0.100 g, 0.95 mmol) was added through a high dilution condenser–thimble–dropping funnel combination. The mixture was refluxed for an additional 12 h, the solvent was evaporated under vacuum, and the residue was shaken with 100 mL of CH_2Cl_2 and 100 mL of H_2O. The water layer was extracted with three 30-mL portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under vacuum to give 0.264 g of crude material that was chromatographed on a 100-Å gel permeation column in CH_2Cl_2. Fraction A, retention volume 192 mL, contained little compound, whereas fraction B, retention volume 215 mL, contained 0.156 g (54%) of **6**, which was submitted to molecular distillation (200 °C at 4 × 10^{-5} mm), mp 123–126 °C; ^{19}F NMR ($CDCl_3$) δ −109.58 (F, 1), −113.51 (F, 2); MS, M^+ 414. Anal. C, H.

49,50,51,52,53,54-Hexafluoro-13,16,19,37,40,43-hexaoxaheptacyclo[43.3.1.1^{2,6}.1^{7,11}.1^{21,25}.1^{26,30}.1^{31,35}]tetrapentaconta-1(49),2,4,6(54),7,9,11(53),21,23,25(52),26,28,30(51),31,33,35(50),45,47-octadecaene (7). Procedure B was applied to 0.171 g of 50% NaH (pentane washed, 3.62 mmol) in 80 mL of THF, 0.295 g (0.75 mmol) of diol **21**, and 0.311 g (0.75 mmol) of diethylene glycol ditosylate in 100 mL of THF. The addition of the diol and ditosylate took 9 h, and refluxing was continued for an additional 32 h. The reaction product was chromatographed on a 100-Å gel permeation column with CH_2Cl_2 as the mobile phase. The fraction with a retention volume of 178 mL, 0.140 g, proved to be crude **7**. The powder was recrystallized from hot absolute ethanol to give 0.057 g (18.4%) of **7**, mp 150–154 °C; ^{19}F NMR ($CDCl_3$) δ −115.87 (F, 2), −120.70 (F, 4); MS, M^+ 828; osmometric molecular weight in CH_2Cl_2, 822. Anal. C, H.

Attempts To Complex Cycle $(CH_3C_6H_2F)_6$ (5). A solution of 10.0 mg of **5** was dissolved in 5.00 mL of $CDCl_3$ to give a 0.0031 M solution. Solutions in $(CD_3)_2SO$ were prepared that were 1.54 M in each of the following salts: $LiClO_4$, $NaClO_4 \cdot H_2O$, $KClO_4$, $RbClO_4$, and $CsClO_4$. In each of six 5-mm NMR tubes was placed 500 μL of the solution of **5** (0.00155 mmol per tube). To each of the five tubes was added 10 μL of a different salt solution, and the six tubes were sonicated for 10 min and allowed to stand for 24 h at ambient temperature. The ^{19}F NMR spectra gave singlets at δ −112.917 (blank tube), −122.963 (Li^+ tube), −112.917 (Na^+ tube), −112.963 (K^+ tube), −112.917 (Rb^+ tube). The ^1H NMR spectrum of each of the six solutions were identical: δ 2.44 (s, 36, CH_3), 7.30 (s, 18, ArH).

Attempts To Detect Complexation of Cycle $(CH_3C_6H_2F)_8$ (8) with Various Solvents. Approximately 2 × 10^{-3} M solutions of **8** in five different solvents were prepared and their ^{19}F NMR spectra determined as temperatures were varied between 258 and 335 K, except for the $(CD_3)_2SO$ solution in which the temperature limits were 315 and 371 K. Although the activation energy barriers for ring inversion at 315 K were within error limits of one another and $^5J_{FF}$ remains constant at 32.5 Hz in all solvents, the fluorine chemical shift differences, $\Delta\delta$ (Hz), at 470.56 MHz were remarkably dependent on solvent for unexplained reasons: 131, CD_2Cl_2 (258 K); 230, $(CD_3)_2SO$ (315 K); 422, $CDCl_3$ (258 K); 465, $(CD_3)_2CO$ (258 K); 244, $CDCl_2CDCl_2$ (258 K).

The ^{19}F NMR spectra at 258 K were simulated with the PANIC program (Bruker software of the Aspect 2000 computer). The $^5J_{FF}$ coupling between fluorine neighbors and the chemical shift difference were varied until the theoretical line shapes matched the experimental spectrum. All other coupling constants were fixed at values less than 1 Hz. The exchange-broadened spectra at 315 K were then simulated with the same program adjusting the chemical shifts and increasing the line width. Rate constants, k, for ring inversion were derived from the line widths due to exchange $\Delta\nu$, with $k = \pi\Delta\nu$. This method is exact as long as exchanging NMR signals do not overlap.[17] There is considerable overlap *within* the ^{19}F triplets but not *between* the two triplets in our system (see Figure 1). We estimate the error in k to be ±50% ($\Delta(\Delta G^{\ddagger})$ ±0.3 kcal mol^{-1}) to account for the systematic errors introduced. A complete line-shape analysis is too complicated for the eight-spin system.

Crystal Structure Determination. The crystals of $(CH_3C_6H_2F)_6$ were prepared by slow evaporation of a CH_2Cl_2 solution. A single crystal (0.35 × 0.40 × 0.50 mm) was used in the diffraction study. The space group is *Pa3* (cubic), four molecules per unit cell, a = 15.621 (4) Å, V = 3812 (2) Å^3, μ = 3.21 cm^{-1}, final R = 0.12, R_w = 0.102, 736 reflections with $F \geq 3\sigma(F)$. Disordered CH_2Cl_2 was present but the rest of the structure refined well. Besides the structural parameters given in the text, additional parameters follow. Deviations of the six fluorine atoms of one molecule from their best plane are ± 0.919 Å. Each CH_3 is bent 0.114 Å out of the best plane of its attached benzene ring. The angle between the normal to the best plane of the benzene ring and the best plane of the six fluorines is 26°.[18]

Registry No. 5, 88229-90-7; **6**, 88229-95-2; **7**, 88229-96-3; **8**, 88229-91-8; **9**, 388-82-9; **10**, 88229-82-7; **11**, 88229-83-8; **12**, 88229-85-0; **13**, 88229-86-1; **15**, 88229-81-6; **16**, 88229-84-9; **17**, 88229-87-2; **18**, 88229-88-3; **19**, 88229-89-4; **20**, 88229-92-9; **21**, 88229-93-0; **22**, 88229-94-1; C_6H_5F, 462-06-6; 4-$CH_3C_6H_4F$, 352-32-9; diethylene glycol, 111-46-6; diethylene glycol ditosylate, 7460-82-4.

Supplementary Material Available: Tables of atomic positional parameters and thermal parameters and of interatomic distances and angles of $(CH_3C_6H_2F)_6$ (2 pages). Ordering information is given on any current masthead page.

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[18] Full publication of the crystallographic study in *Acta Crystallographica* by K. N. Trueblood, E. Maverick, and C. B. Knobler is in preparation.

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trans-Stilbene–Amine Exciplexes. Stereoelectronic Control of Amine Dimer Cation Radical Formation

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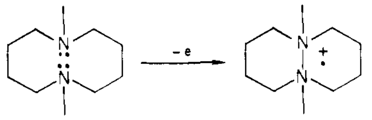
Abstract: The interaction of singlet *trans*-stilbene with several trialkylamines, α,ω-diaminoalkanes, and the bicyclic diamine Dabco in benzene solution has been investigated. The rate constants for fluorescence quenching equal or exceed the rate of diffusion and are not subject to steric hindrance. Exciplex energies and monoamine oxidation potentials show little variation with structure, suggesting that steric destabilization and inductive stabilization counterbalance each other. Intersystem crossing to yield triplet *trans*-stilbene is the predominant exciplex decay pathway at low amine concentrations. At higher amine concentrations, exciplex quenching by ground-state amines occurs and is subjected to a pronounced steric effect in the case of monoamines and a chain-length effect in the case of diiaminoalkanes. On the basis of these effects, exciplex quenching is proposed to occur by the interaction of cation radical and neutral amines to yield a triplex of *trans*-stilbene anion radical and a three-electron, σ-bonded amine dimer cation radical. The energy of this triplex is estimated to be lower than that of triplet *trans*-stilbene.

The interaction of nitrogen lone pairs in monocyclic and bicyclic diamines is destabilizing in the neutral form but stabilizing in the radical cation due to the formation of a three-electron σ bond (eq 1).[1,2] While the formation of diamine monocation radicals from



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