syn-ar,ar'-Difluorometacyclophanes: Strong $^{19}F,^{19}F$ Spin–Spin Interactions Transmitted through Space☆

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Received January 3, 1994

Key Words: Difluorometacyclophanes / *syn*-Metacyclophanes / Through-space F,F spin coupling / X-ray structures

The close approach of the fluorine nuclei in the difluorinated *syn*-[3.3]metacyclophanes **1**, **2** and their [2.2] analogues **3**, **4** leads to strong $^{19}F,^{19}F$ spin–spin interactions which obey a through-space mechanism. The geometries of **1**–**4** were estimated by MM2 molecular mechanics computations, those of **1** and **3** were also determined by X-ray structural analyses. The decrease of the F,F internuclear distance in the series **1**, **2**, **3**, **4** (2.78–2.48 Å) correlates with an increase of *J*(FF) from +42.1 to +99.2 Hz. It follows that, for a given distance *d*(FF), *J*(FF) is up to twice as large as a previous empirical correlation has assumed and even larger with respect to earlier theoretical calculations. Only weak F,F spin interaction occurs in **8**, the *anti* isomer of **4**.

In the usual mechanism of scalar NMR spin–spin coupling, the information of nuclear spin orientation is transmitted by spin polarization of the intervening bonding electrons. If, in the case of a favourable molecular geometry, NMR-active nuclei can approach each other up to the sum of their van der Waals radii or closer, mutual spin–spin interaction occurs even if the nuclei are separated by many bonds. This through-space ("ts") spin coupling[1] is particularly efficient when fluorine nuclei are involved as, e.g., in 1,8-difluoronaphthalenes[2] and in 4,5-difluorophenanthrenes[3] with *J*(FF) = 58.8 Hz and ca. 170 Hz, respectively. Remarkably large ts couplings between ^{31}P nuclei have also been reported recently[4].

There are only a few detailed studies of the geometry dependence of $^{19}F,^{19}F$ ts couplings. However, these have assumed unrealistic molecular geometries[5] (see below) or have treated systems such as fluorinated allyl cations[6], in which the ts contribution to *J*(FF) is, to our minds, debatable. Also an early relationship between *J*(FF) and the internuclear separation *d*(FF) had been derived from, inter alia, geminal and vicinal F,F couplings[7], for which the assumption of predominant through-space spin–spin coupling is unjustified.

Our interest in correlations between molecular structure and spectroscopic properties led us to study the series of structurally closely related compounds, **1**[8], **2**[9], **3**[10] and **4**[10], of the *syn*-metacyclophane family, which we thought to be promising candidates for large F,F ts couplings as relatively small F,F distances are expected. We chose the difluorodithia[3.3]metacyclophane **1** as the starting point. This compound has been known for some time, but has not been investigated with regard to F,F spin–spin interaction. The chemically equivalent fluorine atoms require *J*(FF) to be determined from the ^{13}C satellites in the ^{19}F-NMR spectrum. The ^{19}F signals of the isotopomer, in which one fluorine substituent is connected to ^{13}C, form the AB part of an ABX spectrum ($^{13}C_X-F_A\cdots F_B$) which yields the magnitude of $J(F_AF_B)$ directly (Figure 1a). The coupling constant amounts to a considerable 42.1 Hz. As the fluorine nuclei are separated by eight bonds, which are not well dispositioned for large coupling constants, the through-bond component of *J*(FF) must be small and spin coupling may be assumed to occur almost exclusively through space. Both an X-ray structural analysis (Figure 2) and MM2 molecular mechanics computations[11] were performed to determine the molecular geometry of **1**. The two methods show that the aromatic rings do not lie parallel but are inclined to each other by 13° (MM2) or by 20° (X-ray diffraction) because of the strain imposed by the twofold bridging (Table 1). Thus the C–F bonds are directed towards each other, and the resulting F,F distance is small: 2.754 Å (X-ray structure) or 2.781 Å (MM2), only slightly larger than twice the van der Waals radius of fluorine (1.35 Å). Another difference between the crystal structure of **1** and the geometry calculated by MM2 (for the gas phase) is the size of the angle θ by which the aromatic rings are rotated relative to each other about the axis connecting their midpoints: 7° in the crystal and 1° according to MM2. Both methods show that the most stable conformation of the twelve-membered

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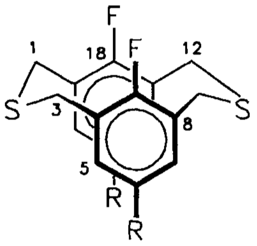
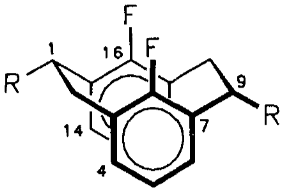
ring, comprising the CH_2SCH_2 bridges and the substituted aromatic carbon atoms, is the crown arrangement depicted in formula **1**.



1: R = H
2: R = *t*Bu



3: R = SMe
4: R = H

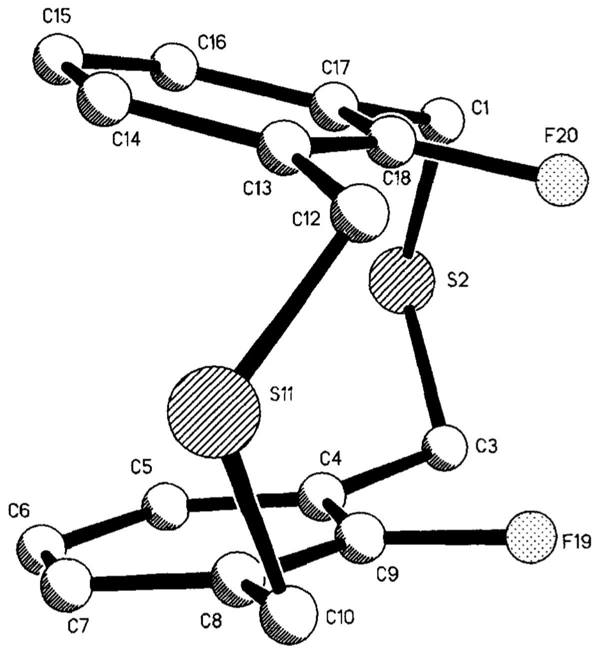


Figure 2. Structure of **1** in the crystal; the distance F19,F20 is 2.754 Å

One conceivable way of forcing the fluorine atoms closer together is by introduction of bulky substituents at their *para* positions. By way of mutual repulsion, such substituents should increase the angle between the aromatic planes and, consequently, diminish *d*(FF). This model consideration was borne out by MM2 calculations that predict an interplanar angle of 27° (relative to 13° for **1**) and a F,F separation of 2.597 Å for the di-*tert*-butyl derivative **2**, so that the preparation seemed worthwhile. We followed a previously reported synthesis[9] but used bis(bromomethyl)- (**5**) instead of bis(chloromethyl)-*tert*-butylfluorobenzene as the coupling partner for dithiol **6**. Contrary to assertions in ref.[9], this reaction does not furnish the *anti* form of **2** but an equilibrium mixture of *syn*-**2** and *anti*-**2**. In $CDCl_3$ solution at room temperature, the conformers are present in a *syn*/*anti* ratio of ca. 8:1 and interconvert slowly on the ^1H-NMR time scale. Coalescence of the *tert*-butyl signals is observed at 378 K (400 MHz, $Cl_2CDCDCl_2$ solution). With an equilibrium constant *K*(*syn*/*anti*) of 3.94 and $\Delta\nu$ = 86.2 Hz (both values extrapolated to 378 K), the interconversion barriers are evaluated[12] as $\Delta G^{\neq}(378\ K)$ = 81.3 (*syn* → *anti*) and 77.0 kJ mol^{-1} (*anti* → *syn*), respectively. The half-life times of the isomers are thus too short for a separation at room temperature[13]. The splitting patterns in the aromatic region of the room-temperature ^1H-NMR spectrum

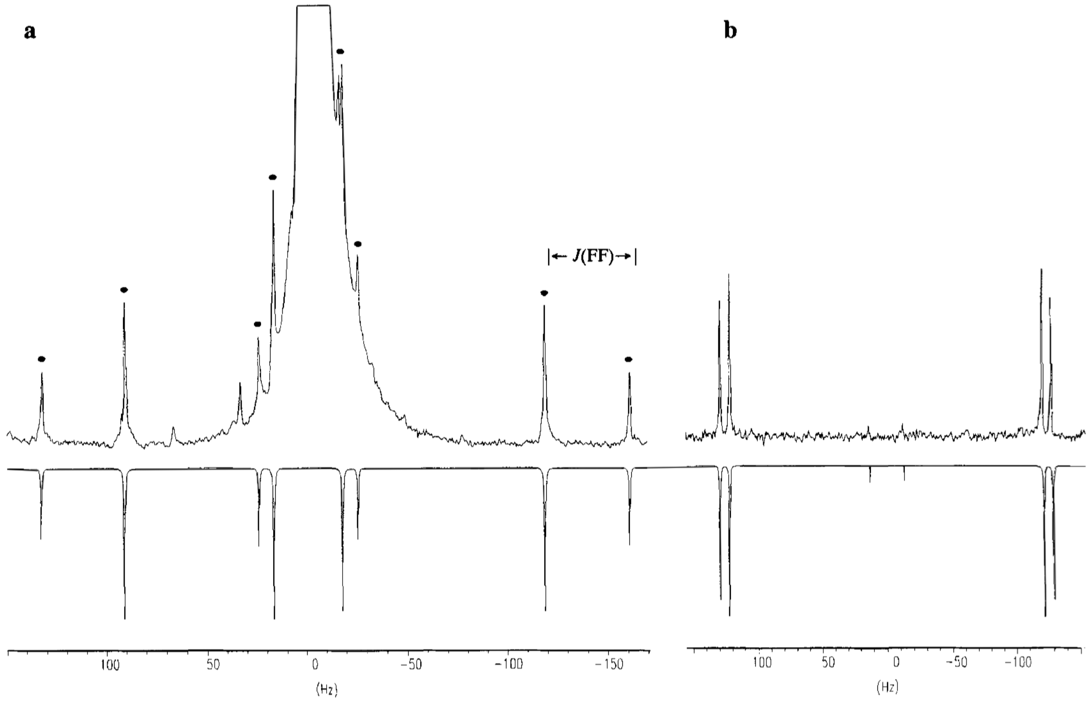


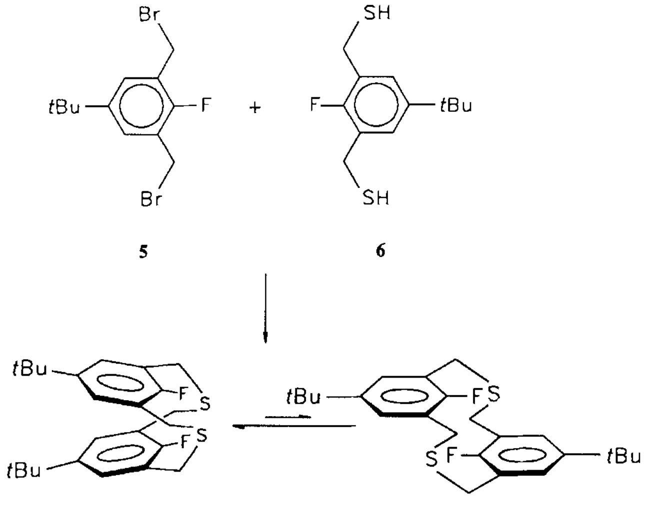
Figure 1. a: ^{13}C satellites in the ^{19}F-NMR spectrum (188 MHz, $CDCl_3$) of **1**, top: experimental, bottom: simulated; the satellites of the [^{13}C-9] isotopomer are marked with dots. – b: ^{13}C-NMR spectrum (50 MHz) of C-9 in **1**, top: experimental, bottom: simulated

Table 1. Nonbonded distances [Å] and angles [°] in **1**−**4** and **8**

Compound	d(FF)	d(CC)[a]	α[b]	θ[c]
1 (X-ray)	2.754	3.114	20	7
1 (MM2)	2.781	3.028	13	1
2 (MM2)	2.597	3.048	27	5
3 (X-ray)	2.540[d]	2.806	24	11
3 (MM2)	2.516	2.874	20	13
4 (MM2)	2.482	2.857	21	12
8 (MM2)	3.553	2.756	0	180

[a] Distance between the fluorine-bearing carbon atoms. − [b] Angle between the best planes through the carbon atoms of each aromatic ring. − [c] Torsion angle F*C*−(ring centre 1)−(ring centre 2)−*C*F. − [d] Mean distance for the two independent molecules.

(Figure 3) are instructive since they immediately suggest a large F,F coupling in the *syn* isomer. While the resonance of the *anti* conformer consists of a simple doublet with ^4J(FH) = 6.6 Hz, as expected for a first-order A_2X spectrum, the corresponding signal of the *syn* conformer is second order (apparent triplet of 3.4 Hz spacing), because the strong F,F coupling makes the protons (and the fluorine nuclei) of the two aromatic rings magnetically non-equivalent ($A_2A_2'XX'$ spin system). The ^{13}C satellites of the ^{19}F signal of *syn*-**2** yield J(FF) as 60.5 Hz, almost a 50% increase with respect to that of **1**, in line with the considerably shortened F,F distance.



5 **6**

syn-**2** *anti*-**2**

The magnetic non-equivalence mentioned prohibits the analysis by first-order rules of all ^{13}C and ^{1}H signals in all of the symmetrical compounds **1**−**4** that display splitting by ^{19}F. Thus, the apparent doublet of doublets (at low signal/noise ratio) of the ^{13}C-9 signal in **1**, for which 251.5 and 7.8 Hz splittings were reported[8c], is in fact the 6-line X part of an ABX spectrum (Figure 1b), and proper analysis yields ^{19}F,^{13}C coupling constants of −244.7 and +0.3 Hz. Also, the interpretation of the ^{1}H-NMR spectrum of **2** in ref.[9] requires correction.

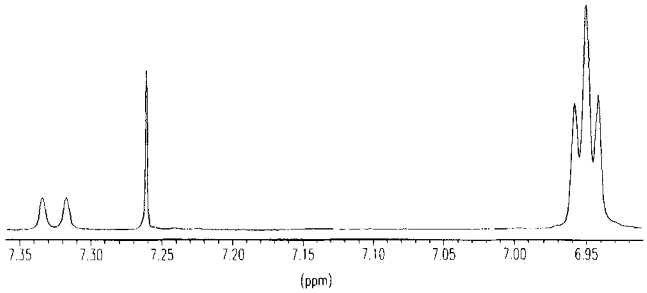


Figure 3. Aromatic region of the ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of *syn*- (δ = 6.95) and *anti*-**2** (δ = 7.33)

Another way to decrease d(FF) relative to that of **1** is to shorten the cyclophane bridges.The [2.2]metacyclophane derivatives **3** and **4** were available from an earlier study[10]. Compound **3** with equatorial SCH_3 groups at the bridges was suitable for an X-ray crystal-structure analysis (Figure 4). Two independent molecules are observed in an asymmetric unit, the distances between the fluorine atoms being 2.548 and 2.531 Å, respectively. The MM2 force-field computation gave d(FF) as 2.516 Å. The F,F coupling constant, 89.3 Hz, is more than twice as large as that of **1**. The shortest F,F contact, 2.482 Å, in the series **1**−**4** was found, by MM2, for *syn*-8,16-difluoro[2.2]metacyclophane (**4**) itself. This molecule also displayed the strongest F,F interaction, 99.2 Hz, missing the 100 Hz limit by only a very narrow margin.

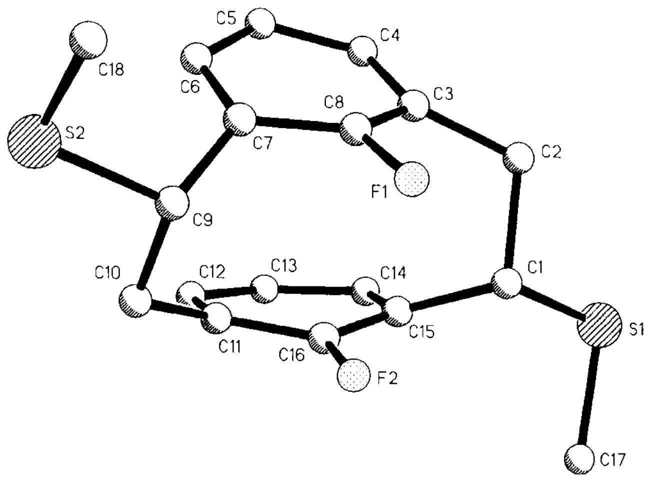


Figure 4. Structure of **3** in the crystal; only one of two molecules in an asymmetric unit is shown; the distance F1,F2 is 2.531 Å in one molecule and 2.548 Å in the other

The relationship between the through-space J(FF) and the internuclear F,F distance was investigated theoretically some time ago by Buckingham and Cordle[14]. Soon thereafter, Hilton and Sutcliffe[1a] pointed out that, for a given distance d(FF), the theoretical values are much too small. They later proposed[5] an "empirical relationship", $J(\mathrm{FF}) = 6800 \exp[-1.99 \cdot d(\mathrm{FF})]$ where d(FF) is measured in Å. In Figure 5, we compare our findings with those of ref.[5] and ref.[14]. As X-ray structural data are not available for the full set of compounds studied, the experimental *J*(FF) values in **1**–**4** are plotted against the internuclear distances *d*(FF) computed with the MM2 method [curve (a)]. For the same set of F,F distances, "empirical" coupling constants were calculated from the equation of Hilton and Sutcliffe[5] [curve (b)]. Finally, curve (c) connects *J*(FF) values for distances of 2.4, 2.6 and 2.8 Å as estimated theoretically by Buckingham and Cordle[14]. The comparison shows that, relative to our experimental findings, the theoretical values are too small by a factor of at least ten, but it becomes clear that the "empirical relationship"[5] also has to be revised. The sizes of the coupling constants predicted by this relationship are approximately only half as large as the experimental ones. The reason for this underestimation lies in the standard geometries that the authors assumed for the compounds from which they derived their equation. One of their model compounds was perfluoro-4-isopropylpyridine in the most stable rotational conformation, **7**. The close approach of 3-F and 4α-F in the standard geometry of **7** would lead to very unfavourable nonbonded interactions. However, at the expense of very little energy, the molecule can respond by widening the bond angles (cf. ref.[15] for the analogous case of 2-isopropylmesitylene) and/or changing the torsion angles[16] to increase the nonbonding F,F distances and efficiently reduce the strain energy. Hence, the actual molecular structure will not be well approximated by the standard geometry. As the *d*(FF) values on which curve (b) in Figure 5 is based are too small, this curve should be shifted to the right; it would then become more similar to curve (a) derived by us.

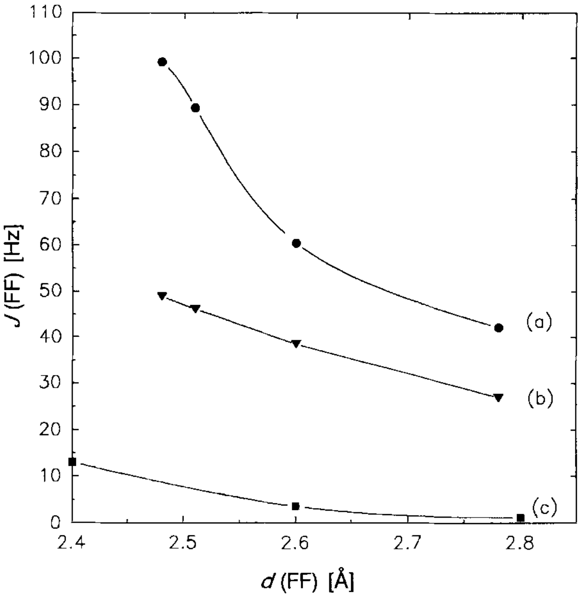
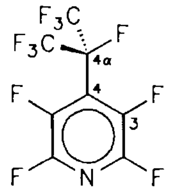


Figure 5. Dependence of the F,F coupling constants in **1**–**4** upon the distance *d*(FF): (a) experimental values plotted against the distances computed with MM2(91); (b) "empirical relationship" according to Hilton and Sutcliffe[5]; (c) theoretical values by Buckingham and Cordle[14]

As the counterpart of **4**, we have also studied its *anti* isomer **8**[17]. As expected, the F,F distance is large [3.553 Å (MM2)] and *J*(FF) small (3.2 Hz). Because of the small magnitude of this coupling we do not claim that it follows a through-space mechanism.



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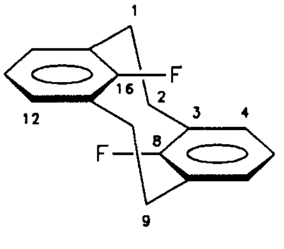

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Theoretical calculations of ^{19}F,^{1}H and ^{19}F,^{13}C ts couplings[18] have shown that the sign of a coupling constant can change with the relative orientation of the C–H and C–F bonds. In the cases of F,F ts coupling described earlier[2,3], the parts of the molecules carrying the C–F bonds were approximately situated in a common plane; in **1**–**4**, however, they lie (ideally) in parallel planes; in **8**, moreover, the C–F bonds are arranged in an antiparallel fashion. We were interested whether the sign of *J*(FF) is affected by the change of the relative orientation of the C–F bonds and therefore determined the sign of *J*(FF) in **1**, **4** and **8** by means of $^{13}C\{^{1}H_{BB},^{19}F_{sel.}\}$ triple-resonance experiments. The irradiation experiments were simulated with the program DOR/DORUOM[19] for both signs of *J*(FF). According to these simulations, *J*(FF) is positive relative to a negative ^{1}J(FC) in all three compounds. Positive signs had also been found for other F,F couplings for which the ts mechanism prevails, such as ^{4}J(FF) in 2-fluorobenzotrifluorides[20] and 1,8-difluoronaphthalene[21] and ^{5}J(FF) in difluoro[2-(trifluoromethyl)phenyl]phosphane[22]. So the altered relative orientation of the C–F bonds is not accompanied by a sign change of *J*(FF).

We conclude that for a given distance *d*(FF) the spin–spin coupling *J*(FF) transmitted through space is up to twice as large as so far assumed, at least for the range of distances studied here (2.48–2.78 Å), and remarkably strong through-space coupling is already observed at an F,F distance of twice the fluorine van der Waals radius. Finally, it is conceivable that *d*(FF) is not the only geometrical factor determining *J*(FF) and that the relative orientation of the F–C bond vectors is also of importance. To test this conjecture would require the study of model compounds that possess similar F,F distances but different F–C bond orientations. This requirement is difficult to meet.

This work was supported by the *Fonds der Chemischen Industrie*, Frankfurt/Main, and the *National Sciences and Engineering Research Council of Canada*.

Experimental

Melting points are uncorrected. – NMR: The solvent was $CDCl_3$ in all cases. Instruments: Bruker AM 400 (^{1}H: 400.1 MHz, internal standard: TMS), Bruker AC 200 (^{13}C: 50.3 MHz, internal standard: $CDCl_3$, $\delta = 77.05$; ^{19}F: 188.3 MHz, substitutive internal standard: $CFCl_3$ in $CDCl_3$). The *syn*/*anti* relationship of methylene protons relative to a fluorine substituent was derived from reciprocal NOEs with their *ortho* protons. Multiplicities reported with the ^{13}C-NMR data refer only to spin coupling with fluorine. The degree of substitution of the carbon atoms was in all cases determined by DEPT experiments. The results were compatible with the spectral assignments given and are not stated explicitly. For the determination of coupling constants from ^{13}C or ^{19}F spectra digital resolutions of at least 0.1 Hz per data point were generally used. Gaussian multiplication and zero filling were also applied. Triple-resonance experiments: Bruker AM-300, ^{13}C measurement (75.5 MHz) with ^{1}H broadband decoupling (300.1 MHz, filter: ^{19}F stop/^{1}H pass). The selective ^{19}F irradiation frequency (282.4 MHz) was generated with a PTS 160 MHz synthesizer and a frequency doubler and fed into the ^{1}H decoupling coil with a directional coupler after filtering (^{19}F pass/^{1}H stop) and attenuation (Texscan attenuator with 1 dB step size). Simulation of the triple-resonance spectra was carried out with the program DOR/DORUOM[19] both for a positive and a negative sign of J(FF). – MS: Finnigan MAT 8430.

syn-9,18-Difluoro-2,11-dithia[3.3]metacyclophane (**1**)[8]: ^{1}H NMR: $\delta = 6.97$ [$A_2A'_2$MM'XX', "quint", J(5-H,6-H) = 7.6 Hz, 5-H], 6.69 (t, 6-H), 4.34 (d, J = 15.0 Hz, H_{syn} of CH_2), 3.41 (d, J = 15.0 Hz, H_{anti} of CH_2). – ^{13}C NMR: $\delta = 158.6$ [6 lines, ABX, J(FC) = −244.7 and +0.3 Hz, C-9], 129.8 ["t", ΣJ(FC) = 3.8 Hz, C-5], 125.1 ["dd", ΣJ(FC) = 15.6 Hz, C-4), 124.2 ["t", ΣJ(FC) = 4.3 Hz, C-6], 29.2 ["t", ΣJ(FC) = 5.1 Hz, CH_2]. – ^{19}F NMR: $\delta = -125.6$, J(FF) = +42.1 Hz.

1,3-Bis(bromomethyl)-5-tert-butyl-2-fluorobenzene (**5**): A mixture of 31.7 g (176 mmol) of 5-*tert*-butyl-2-fluoro-1,3-dimethylbenzene[9], 64.1 g (360 mmol) of *N*-bromosuccinimide and 0.35 g of azobis(isobutyronitrile) in 350 ml CCl_4 is heated under reflux for ca. 2 h by irradiation with a 600-W bulb. After cooling to room temperature, succinimide is filtered off, the solvent removed by distillation and the remaining solid recrystallized twice from petroleum ether. Yield 18.3 g (31%), m.p. 77.5–78°C. – ^{1}H NMR: $\delta = 7.34$ [d, J(FH) = 6.8 Hz, 4-H], 4.51 (br. s, CH_2), 1.31 (s, *t*Bu). – ^{13}C NMR: $\delta = 156.9$ [d, J(FC) = 252.3 Hz, C-2], 147.7 [d, J(FC) = 4.5 Hz, C-5), 128.8 [d, J(FC) = 3.1 Hz, C-4), 124.8 [d, J(FC) = 14.3 Hz, C-1], 34.5 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$), 25.9 (s, CH_2). – ^{19}F NMR: $\delta = -126.2$. – MS (70 eV); *m*/*z*: 336/338/340 (7/12/7) [M^+], 321/323/325 (11/21/11) [$M^+ - CH_3$], 257/259 (100/99) [$M^+ - Br$], 179 (11), 178 (30) [$M^+ - 2\,Br$], 163 (17). – $C_{12}H_{15}Br_2F$ (338.1): calcd. C 42.64, H 4.47, Br 47.27; found C 42.59, H 4.36, Br 47.29.

syn-6,15-Di-tert-butyl-9,18-difluoro-2,11-dithia[3.3]metacyclophane (**2**)[9]: The synthesis was carried out similarly to ref.[9] by using **5** as the starting material instead of the bis(chloromethyl) derivative. The product was purified by column chromatography [Kieselgel 60, 63–200 µm (Merck), petroleum ether/CH_2Cl_2 (2:1)] and recrystallized from CH_2Cl_2/2-propanol (ca. 5:1), m.p. 113–114°C (ref.[9] 108–111°C). – ^{1}H NMR: *syn* isomer: $\delta = 6.95$ ($A_2A'_2$XX', "t", N = 6.7 Hz, H_{ar}), 4.32 (d, J = 15.0 Hz, H_{syn} of CH_2), 3.41 (br. d, J = 15.0 Hz, H_{anti} of CH_2), 1.14 (s, *t*Bu); *anti* isomer: $\delta = 7.33$ [d, J(FH) = 6.6 Hz, H_{ar}], 3.74 (d, J = 14.0 Hz, H_{syn} of CH_2), 3.44 (br. d, J = 14.0 Hz, H_{anti} of CH_2), 1.35 (s, *t*Bu). – ^{13}C NMR: *syn* isomer: $\delta = 156.8$ [6 lines, ABX, J(FC) = −243.4 and +0.3 Hz, C-9], 146.4 ["t", ΣJ(FC) = 4.1 Hz, C-6], 126.3 ["t", ΣJ(FC) = 3.6 Hz, C-5], 124.6 ["dd", ΣJ(FC) = 15.5 Hz, C-4], 34.2 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$), 29.8 ["t", ΣJ(FC) = 4.5 Hz, CH_2]; *anti* isomer: $\delta = 158.0$ [d, J(FC) = 247.1 Hz, C-9], 146.7 [dd, J(FC) = 4.2 and 0.9 Hz, C-6], 127.6 [dd, J(FC) = 3.5 and 1.0 Hz, C-5], 122.3 [dd, J(FC) = 14.9 and 0.5 Hz, C-4], 34.4 (s, *C*Me$_3$), 31.4 (s, C*Me*$_3$), 25.7 [d, J(FC) = 4.6 Hz, CH_2]. – ^{19}F NMR: $\delta = -129.0$, J(FF) = 60.5 Hz (*syn*); −125.6 (*anti*), J(FF) not resolved.

syn-1,9-di-eq-Bis(methylthio)-8,16-difluoro[2.2]metacyclophane (**3**)[10]: ^{1}H NMR: $\delta = 7.05-7.01$ (m, 6-H), 6.50 (t, J = 7.5 Hz, 5-H), 6.38–6.34 (m, 4-H), 4.92 (t, 1-H_a), 3.83 (dd, 2-H_a), 2.18 (s, SCH_3), 2.11 (dd, 2-H_e), J(1-H_a,2-H_a) = 8.5, J(1-H_a,2-H_e) = 8.5, J(2-H_a,2-H_e) = 13.7 Hz; assignment from NOEs between aromatic and bridge protons. – ^{13}C NMR: $\delta = 160.5$ [6 lines, ABX, J(FC) = −252.8 and +0.4 Hz, C-8], 130.9 ["t", ΣJ(FC) = 6.4 Hz, C-4], 127.4 ["dd", ΣJ(FC) = 20.3 Hz, C-3 or C-7], 127.2 ["dd", ΣJ(FC) = 14.4 Hz, C-7 or C-3], 126.9 ["t", ΣJ(FC) = 3.6 Hz, C-6], 124.4 ["t", ΣJ(FC) = 4.4 Hz, C-5], 43.4 ["t", ΣJ(FC) = 6.6 Hz, C-1], 40.6 ["t", ΣJ(FC) = 2.5 Hz, C-2], 16.2 (s, SCH_3). – ^{19}F NMR: $\delta = -106.8$, J(FF) = 89.3 Hz.

syn-8,16-Difluoro[2.2]metacyclophane (**4**)[10]: ^{1}H NMR: $\delta = 6.37$ (m_c, H_{ar}), 3.49 (m_c, AA'XX', N = 8.6 Hz, H_{syn} of CH_2), 2.60 (m_c, AA'XX', N = 8.6 Hz, H_{anti} of CH_2). – ^{13}C NMR: $\delta = 160.9$ [6 lines, ABX, J(FC) = −251.9 and +0.5 Hz, C-8], 129.4 ["t", ΣJ(FC) = 5.5 Hz, C-4], 126.9 ["dd", ΣJ(FC) = 18.5 Hz, C-3], 123.9 ["t", ΣJ(FC) = 4.4 Hz, C-5], 29.1 ["t", ΣJ(FC) = 4.6 Hz, C-1]. – ^{19}F NMR: $\delta = -105.9$, J(FF) = +99.2 Hz.

anti-8,16-Difluoro[2.2]metacyclophane (**8**)[17]: ^{1}H NMR: $\delta = 7.13-7.01$ (m, H_{ar}), 2.81 (m_c, AA'BB', H_{anti} of CH_2), 2.67 (m_c, AA'BB', H_{syn} of CH_2). – ^{13}C NMR: $\delta = 160.4$ ["dd", ABX, J(FC) = −246.9 and +3.2 Hz, C-8], 128.7 [6 lines, ΣJ(FC) = 7.0 Hz, C-4], 127.6 [6 lines, J(FC) = 18.2 and 0.5 Hz, C-3], 124.8 [5 lines, ΣJ(FC) = 4.0 Hz, C-5], 34.0 [ca. "dd", ΣJ(FC) = 0.3 or 0.6 Hz, CH_2]. – ^{19}F NMR: $\delta = -124.0$, J(FF) = +3.2 Hz.

Crystal Data for **1**[23]: $C_{16}H_{14}F_2S_2$, M_r = 308.40 g mol^{-1}, colourless, crystal dimensions 0.21 × 0.37 × 0.47 mm, monoclinic space group $P2_1/n$ (no. 14), $a = 10.055(2)$, $b = 16.334(2)$, $c = 8.999(2)$ Å, $\beta = 106.54(2)°$, $V = 1416.8(3)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.446$ g cm^{-3}, $\rho_{found} = 1.426$ g cm^{-3}, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 3.78 cm^{-1}, 2736 reflections with $2\Theta \leq 50°$ were recorded with a Picker 4-circle diffractometer, and the structure was solved by using a least-squares refinement, $R = 0.0516$, $R_w = 0.0547$ $\{w = 1/[\sigma^2(F) + 0.001F^2]\}$, 2495 independent reflections were used to refine 238 parameters, all the non-hydrogen atoms were refined as anisotropic scatterers, and all the hydrogen atoms were found and refined isotropically.

Crystal Data for **3**[23]: $C_{18}H_{18}F_2S_2$, M_r = 336.46 g mol^{-1}, colourless, crystal dimensions 0.30 × 0.95 × 0.45 mm, triclinic space group $P\bar{1}$ (no. 2), $a = 13.658(2)$, $b = 7.579(2)$, $c = 16.440(2)$ Å, $a = 95.88(2)°$, $\beta = 97.74(1)°$, $\gamma = 80.35(2)°$, $V = 1657$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.349$ g cm^{-3}, $\rho_{found} = 1.35$ g cm^{-3}, $\lambda = 1.542$ Å, μ(Cu-K_α) = 29.9 cm^{-1}, 4484 reflections with $2\Theta \leq 110°$ were recorded with an Enraf-Nonius CAD4 automated diffractometer, and the structure was solved by using a least-squares refinement (SHELX76), $R = 0.0985$, $R_w = 0.1282$ $\{w = 1/[\sigma^2(F) + 0.001F^2]\}$, 2775 independent reflections were used to refine 397 parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. Two molecules in an asymmetric unit differ by rotation of one SMe group by 7°.

☆ Dedicated to Prof. Dr. *Albrecht Mannschreck* on the occasion of this 60th birthday.

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