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Spin–Spin Interactions Across the “Cove” in the (*Z*) and (*E*) Isomers of 1,1′-Difluoro-9,9′-bifluorenylidene

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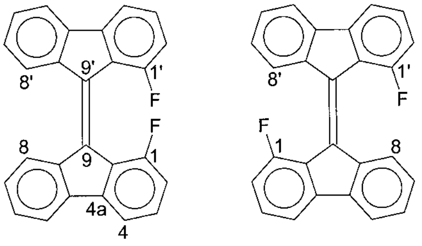
Dedicated to Professor Henning Hopf on the occasion of his 65th birthday

Keywords: Through-space F,F spin–spin coupling / NMR spectroscopy / X-ray diffraction / Density functional calculations / Strained molecules / Configuration determination / Compliance constants

In the (*Z*) isomer, but not in the (*E*) isomer of title compound **1**, moderate $^{19}F,^{19}F$ spin–spin coupling across the "cove" is observed [J(F,F) = 11.0 Hz], which is deemed to obey a through-space mechanism. The coupling between the isochronous fluorine nuclei of **1Z** causes second-order effects in the ^1H, ^{13}C and ^{19}F NMR spectra of this compound and allows its easy distinction from the (*E*) isomer. A B3LYP/6-31+G(d) calculation of **1Z** as an isolated molecule was carried out which gave a non-bonded F,F distance d(F,F) of 2.711 Å and an angle between the two C–F bond vectors of 34.1°. The computed F···F compliance constant of 6.96 Å/mdyn points to a very weak interaction. According to our previous correlation between d(F,F) and through-space J(F,F), the F,F distance in **1Z** would be expected to go along with a coupling constant of ca. 46 Hz. This discrepancy between prediction and experiment gives support to our earlier presumption that a simple d(F,F)/J(F,F) correlation may not sufficiently describe through-space couplings and that an angular factor should also be taken into account. An X-ray diffraction study of **1Z** resulted in an F,F distance of 2.638 Å and an angle between the C–F bonds of 36.4°, in fair agreement with the MO calculation. The rigidity of the (*Z*) isomer was studied using theoretical compliance constants.

Introduction

This paper deals with the NMR, MO computational and X-ray diffractional investigation of the (*Z*) isomer of 1,1′-difluoro-9,9′-bifluorenylidene (**1Z**) and of its (*E*) isomer (NMR only). For the reasons given below, our main interest lies in the expected $^{19}F,^{19}F$ spin–spin interaction across the "cove"[1] in **1Z**, which is thought to operate through space. In the past we have studied a considerable number of difluorinated cyclophanes (with one fluorine substituent per aromatic ring) in order to elucidate the geometrical dependence of the efficiency of through-space spin–spin coupling between two fluorine nuclei (Scheme 1).[2]



1Z **1E**

Scheme 1.

The series of compounds investigated earlier comprised mainly difluoro[2.2]metacyclophanes **2** and **3**[2] and pseudo-*gem*-difluoroparacyclophanes **4** and **5**.[3] These compounds were selected because molecular mechanics computations and/or X-ray diffraction studies had shown that the fluorine atoms in these molecules are very close in space with non-bonded distances d(F,F) varying between 2.42 and 3.17 Å. Because of the large number of chemical bonds between the fluorine atoms (seven or eight) and their nature and arrangement, through-bond contribution to F,F spin–spin coupling was deemed negligible[4,5] so that the experimental coupling constants J(F,F) should fully obey a through-

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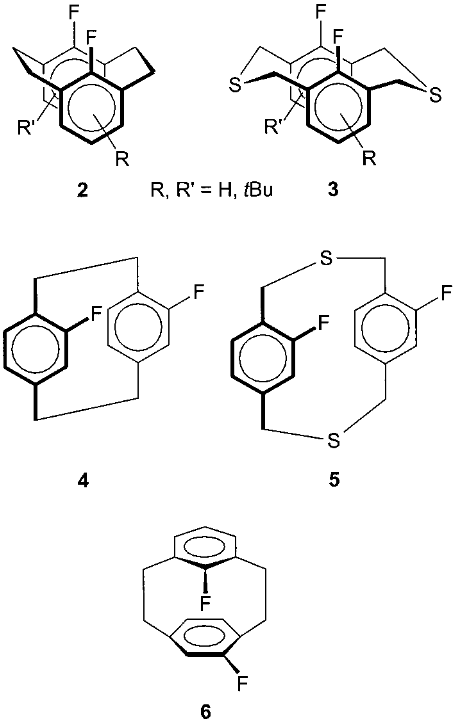
space coupling mechanism. We derived[2] an exponential dependence of $J(\mathrm{F,F})$ upon $d(\mathrm{F,F})$ [Equation (1)], where $J(\mathrm{F,F})$ is expressed in Hz and $d(\mathrm{F,F})$ in Å.[6]

$$J(\mathrm{F,F}) = 275000\,\exp[-3.211\,d(\mathrm{F,F})] \qquad (1)$$

syn-Difluoro[2.2]metaparacyclophane **6** (Scheme 2), however, did not obey Equation (1).[7] It possesses a computed F,F distance of 3.017 Å, for which Equation (1) predicts a $J(\mathrm{F,F})$ value of 17.1 Hz. But the experiment furnished a coupling constant of only 1.9 Hz. We speculated that this discrepancy could be due to the substantial angle between the two F–C bond vectors (30° in the ideal undistorted structure with parallel aromatic rings) while this is much smaller in the other compounds investigated (0° in the idealized structures). Such an angular dependence of through-space $J(\mathrm{F,F})$ couplings has recently also been supported by theoretical calculations.[8–13]



Scheme 2. Compounds studied earlier with regard to through-space F,F coupling.

In order to shed more light onto this problem, we turned our attention to 1,1′-difluoro-9,9′-bifluorenylidene (**1**). This compound is known, as a mixture of (*E*) and (*Z*) isomers, from the work of Agranat and colleagues.[14,15] 9,9′-Bifluorenylidenes carrying no or only small substituents in the 1,1′-positions possess rather large barriers to (*E*)/(*Z*) isomerization.[16] The lower limit of $\Delta G^{\ddagger}$ for **1** is 94 kJ·mol^{-1} at 220 °C as determined by attempted coalescence of the ^{19}F NMR signals of **1E** and **1Z**.[17] Hence, difficulties caused by rapid isomer equilibration are not to be expected. An inspection of a Dreiding molecular model of **1Z** showed that the F–C bond vectors are not antiparallel to one another as a consequence of the five-membered central rings of the fluorenylidene subunits and that there must be a substantial amount of twist about the central C=C bond in the conformational ground state in order to avoid unfavorable nonbonded interactions between the 1- and 1′-fluorine atoms and between the 8- and 8′-hydrogen atoms. Thus, **1Z** was believed to be a good model for through-space F,F couplings in a compound with skew F–C bonds.

Results and Discussion

The synthesis of **1** according to the literature[15] could be reproduced very well and yielded a mixture of **1Z** and **1E**, the desired (*Z*) isomer being the major product. From the ^{1}H NMR spectrum of their isomeric mixture, Agranat et al.[14] had derived a (*Z*)/(*E*) ratio of 43:57, but apparently failed to notice that this was contradicted by their (correct) assignment of the ^{19}F NMR spectrum, which showed [(*Z*)]/[(*E*)] = 4:3. Given this and in view of the low magnetic field strength at which the spectra in ref.[14] had been recorded, it seemed appropriate to us to fully assign and analyze the ^{1}H, ^{13}C and ^{19}F NMR spectra of both isomers. Our attempts to separate the isomers by recrystallization or chromatography were unsuccessful but serendipity would have it that a crystal for X-ray diffraction was isolated which consisted of **1Z** only (see below). The NMR analyses were performed on the isomeric mixture.

{NMR Spectra of 1Z and 1E

Isomers **1Z** and **1E** can easily be distinguished in their NMR spectra. As the ^{19}F nuclei in **1Z** have identical shifts and are coupled to one another, there is magnetic nonequivalence of the fluorine nuclei and of the pairs of corresponding protons in the two fluorine-bearing aromatic rings. The resulting second-order spin system is of the type $[\mathrm{AMXF}]_2$ (A, M, X = ^{1}H; F = ^{19}F). As a consequence, complex splitting patterns show up for the ^{1}H-coupled ^{19}F signal at $\delta = -102.5$ ppm (Figure 1), which must therefore belong to **1Z**, and for protons 2,2′-H and 3,3′-H, which have large $J(\mathrm{F,H})$ coupling constants (Figure 2). Protons 4,4′-H show only some line broadening compared to their counterparts in **1E** because $^{5}J(\mathrm{F,H})$ is small. By way of contrast, the ^{1}H and ^{19}F NMR spectra of the fluorine-bearing aromatic ring of **1E** are of the first-order type. In the absence of ^{1}H decoupling, the ^{19}F signal of **1E** at $\delta = -97.2$ ppm is a clean ddd with coupling constants $^{3}J(\mathrm{F,H}) = 10.7$, $^{4}J(\mathrm{F,H}) = 4.8$ Hz and a through-space interaction $^{\mathrm{ts}}J(1\text{-F},8'\text{-H})$ of 8.2 Hz (Figure 1). This latter interaction had been reported to be 7 Hz.[14] The signals for 2-H and 3-H of **1E** are also clean ddd signals that lack the second-order features of the corresponding signals of **1Z** (Figure 2). The ^{1}H NMR spectrum of the **1Z**/**1E** mixture was analyzed iteratively by fitting the full spectral band shape.[18,19] All chemical shifts and coupling constants were allowed to vary in addition to the relative statistical weight of the isomers. The sample investigated had a composition [**1Z**]/[**1E**] of 69:31, close to the composition of the raw product. Although the latter was not analyzed precisely, it is certain that isomer **1Z** is

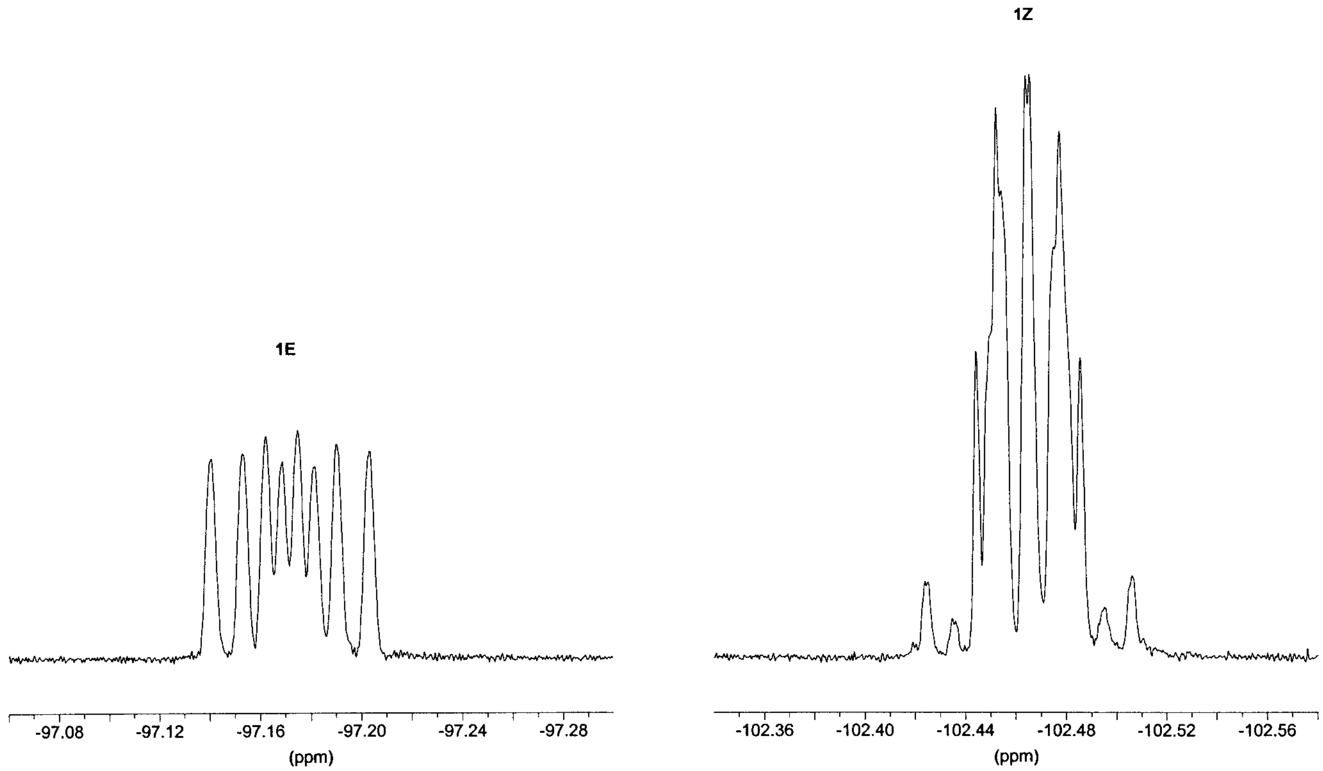


Figure 1. Proton-coupled ^{19}F NMR spectrum at 376 MHz of **1Z/1E** in a ratio of 69:31; solvent $CDCl_3$.

the preferred product of the dimerization of the precursor carbene. The ^{1}H NMR spectra in Figure 2 are the theoretical ones obtained in the iterative fitting. They are shown separately for the isomers and are drawn with comparable intensities for the purpose of clarity. The experimental spectrum of the isomeric mixture and the superposition of the calculated spectra in their proper ratio are contained in the Supporting Information (Figure S1).

Proton-decoupled ^{19}F NMR spectra were also recorded in order to study the ^{13}C satellites from which $J(F,F)$ is most easily determined. These ^{13}C satellites are the AB part of an ABX spin system (A, B = ^{19}F; X = ^{13}C) and the separations of the two outer satellite lines on each side of the "main ^{19}F signal" (i.e. for the $[1,1'\text{-}^{12}C_2]$isotopomer) represent $J(F,F)$. This coupling was found to be 11.0 Hz for **1Z**. No splitting was observed in the satellites of the **1E** signal. From their line width, the F,F coupling in the (*E*) isomer is estimated as <0.5 Hz. All eight theoretical satellite lines in the AB part were observed including the ones close to the ^{19}F–^{12}C line and this allowed us to also determine the isotope effects of ^{13}C upon the ^{19}F chemical shifts and the coupling constants $^{1}J(1\text{-F,C-1})$ and $^{ts}J(1\text{-F,C-1}')$. The size of the one-bond isotope effect, $^{1}\Delta^{19}F(^{13/12}C) = -87.4$ ppb, is in the normal range, cf. the corresponding values in the series monofluorobenzene to hexafluorobenzene (–79 to –98 ppb).[20] The through-space isotope effect is relatively small, $^{ts}\Delta^{19}F(^{13/12}C) = -4.7$ ppb, but too large to be ignored. Like the effect over one bond, it is a shielding effect.

The one-bond F,C coupling constants are practically equal in both isomers, namely –259.8 Hz in **1Z** and –260.2 Hz in **1E**. A large through-space F,C coupling of 9.8 Hz is observed in **1E** between 1-F and C-8′ and smaller ones between 1-F and C-7′ (1.0 Hz), C-8′a (3.6 Hz), C-9′ (ca. 3.2 Hz) and C-4′b (0.5 or, less likely, 2.9 Hz), see Scheme 3. As far as **1Z** is concerned, the analysis of the ABX spectrum mentioned above yields two solutions with identical $^{1}J(F,C)$ values and $^{ts}J(1\text{-F,C-1}')$ values of +4.4 Hz and –5.3 Hz. The X parts of the theoretical spectra calculated from the two solutions differ only slightly in the relative intensities of the satellites close to the main ^{19}F line (Supporting Information, Figure S2). In the experimental spectrum these intensities are falsified by overlap with the main ^{19}F line and with other satellites and by the effect of the Gaussian multiplication applied to the free induction decay to improve the resolution of the spectrum. Hence we cannot state which of the values of the through-space F,C coupling in question is the correct one. In any case, the absolute value is 4.9 ± 0.6 Hz. Through-space F,C couplings involving other carbon nuclei are not discernible in the ^{13}C NMR spectrum of **1Z**. As the absorptions of all ^{13}C nuclei of **1Z** are the X parts of ABX or AA′X spectra and as the AB or AA′ parts in the ^{19}F NMR spectra are not visible (apart from that of C-1,1′), one can only extract the sum $|J(AX) + J(BX)|$ or $|J(AX) + J(A'X)|$ and not the individual values, see Table 1.

When one compares the chemical shifts of **1Z** and of **1E** with those of the parent compound 9,9′-bifluorenylidene (see Exp. Sect.), one finds a number of expected effects such as shielding of the protons and carbon nuclei *ortho* and *para* to the fluorine substituents etc. It is more instructive to

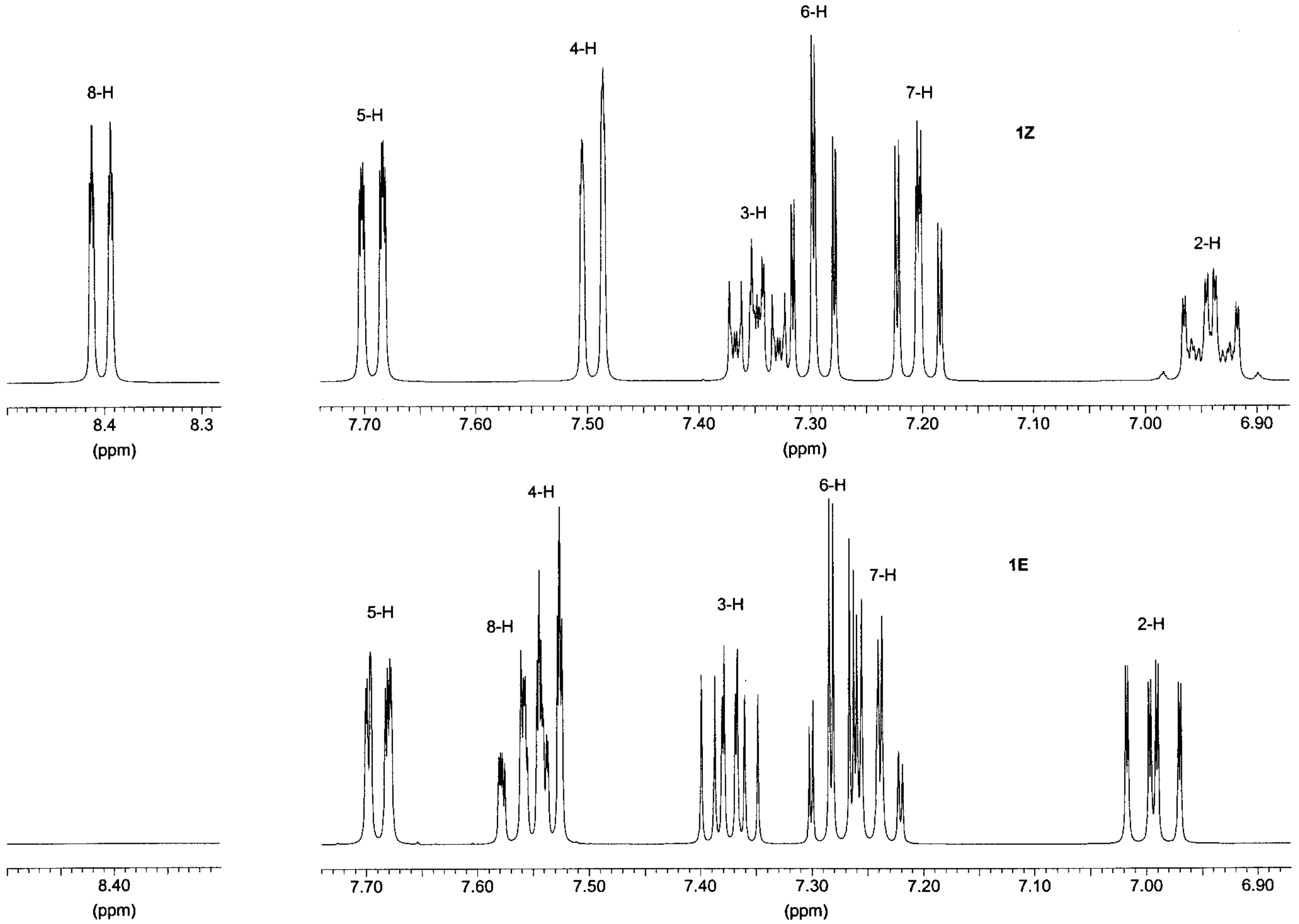
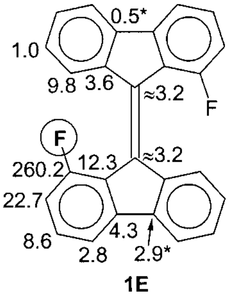


Figure 2. Simulated 400 MHz ^{1}H NMR spectra of **1Z** (top) and of **1E** (bottom) drawn at equal intensities. Note the second-order features of the signals of 2-H and 3-H in the spectrum of **1Z**. For the experimental spectrum of the **1Z**/**1E** mixture, see Figure S1 in the Supporting Information.



Scheme 3. *J*(F,C) coupling constants (absolute values) in **1E** involving the nuclear spin of the encircled fluorine atom. The two values marked with asterisks are interchangeable.

Table 1. ^{13}C NMR spectroscopic data of isomers **1Z** and **1E** (solvent: $CDCl_3$; reference: $CDCl_3$, δ = 77.0 ppm).

Position	δ_C(**1Z**)	δ_C(**1E**)	ΣJ(F,C)(**1Z**) [Hz]	*J*(F,C)(**1E**) [Hz]
1	159.4	159.2	265.2 or 255.5	260.2
2	115.1	115.2	22.9	22.7
3	131.1	131.4	8.7	8.6
4	115.6	116.2	2.4	2.8
4a	142.8	144.3	5.2	4.3
4b	140.7	139.8	2.6	2.9, 0.5
5	120.5	120.0	ca. 0	ca. 0
6	129.1	128.4	ca. 0	ca. 0
7	127.4	127.55	ca. 0	1.0
8	126.7	127.53	ca. 0	9.8
8a	138.8	139.7	ca. 0	3.6
9	137.6	135.4	ca. 0	3.2, 3.2
9a	126.1	124.9	17.8 or 5.4	12.3

compare the chemical shifts of the (*Z*) isomer with those of the (*E*) isomer. Among the ^{1}H chemical shifts, a significant difference is found only for 8-H, which is deshielded by 0.84 ppm in the (*Z*) relative to the (*E*) isomer. As for the ^{19}F nuclei, they exhibit relative deshielding, by 5.29 ppm, in the (*E*) isomer. In other words, both the proton and the ^{19}F nucleus are shielded when the close nucleus in the second half of the molecule is fluorine relative to the case when it is hydrogen. This contrasts with Abraham's finding that the axial proton at C-3 in cyclohexane is substantially deshielded by the introduction of an axial fluorine atom at C-1.[21,22] The complete set of ^{1}H and ^{19}F NMR parameters of **1Z** and **1E** is given in Table 2.

Table 2. ^{1}H and ^{19}F NMR spectroscopic data of isomers **1Z** and **1E** (solvent: $CDCl_3$; references: TMS, CCl_3F).

Position	δ_H(**1Z**)	δ_H(**1E**)	Position	J(**1Z**) [Hz]	J(**1E**) [Hz]
1	–102.5 (δ_F)	–97.2 (δ_F)	1,1′ or 1,8′	11.0 (1,1′)	8.15 (1,8′)
2	6.941	6.994	1,2	11.09	10.66
3	7.348	7.374	1,3	4.43	4.77
4	7.494	7.535	1,4	0.62	0.65
5	7.692	7.689	2,3	8.13	8.17
6	7.296	7.280	2,4	0.85	0.85
7	7.204	7.241	3,4	7.43	7.42
8	8.403	7.558	5,6	7.62	7.58
			5,7	1.16	1.21
			5,8	0.68	0.62
			6,7	7.35	7.24
			6,8	0.96	1.04
			7,8	7.95	7.97

The ^{13}C NMR chemical shifts also differ little between the isomers. The largest shift differences, $\Delta\delta = \delta_Z - \delta_E$, were found for C-9, C-9a, and C-4a with 2.2, 1.2 and –1.5 ppm, respectively. We tentatively attribute them to different degrees of twisting in the isomers and, hence, different C(9)=C(9′) π-bond order and degree of of conjugation. As the absolute magnitudes of all other ^{13}C shift differences are smaller than 1 ppm, direct steric influences are similar in the isomers and, probably, rather small.

The through-space J(F,F) coupling constant of 11.0 Hz in **1Z** is rather small relative to the value of ca. 46 Hz predicted by means of Equation (1). As this equation was derived from the series of compounds **2**–**5** in which the two C–F bonds of interest are arranged in a more or less parallel fashion, **1Z**, beside **6**, constitutes another example which shows that through-space J(F,F) coupling is governed simultaneously by distance and angular factors. It is therefore desirable to design and study further difluorinated molecules of varying geometries in order to obtain experimental data that describe more fully the geometry dependence of through-space J(F,F).

Theoretical Calculations of the Molecular Structure of 1Z

Since structural details of **1Z** were not known at the beginning of our study, we performed theoretical calculations using the hybrid HF-DFT method b3lyp[23] as implemented in the Gaussian 03[24] set of programs, which was used for all our computations. The basis set was of double-zeta quality with polarized basis functions on non-hydrogen atoms augmented with one set of diffuse functions [6-31+G(d)] for a proper description of nonbonded F···F interactions. The most important geometrical parameters of the optimized equilibrium structure were 1.382 Å, 2.711 Å and 34.1° for the C=C bond length, the F···F distance and the C=C torsion, respectively. Using the theoretical nuclear magnetic shielding tensor computed at the same level of theory, we calculated the ^{19}F chemical shift for **1Z** at δ = –104 ppm (GIAO) as compared to the experimental value of δ = –102.5 ppm. We further performed compliance constant[25] calculations to estimate the structural rigidity of **1Z** especially with respect to torsional dynamics. As compliance constants measure the displacement of a specific internal coordinate due to an external force (units: Å/mdyn or rad/mdyn), they directly indicate potential structural distortions in condensed phases. According to our calculations, the B3LYP/6-31+G(d) compliance constant for the C=C bond in **1Z** is 0.140 Å/mdyn which is in line with a pronounced weakening of the C=C double bond in comparison with the C=C bond in ethene (compliance constant: 0.112 Å/mdyn). This weakening – due to the partially broken π-bond – in combination with a weak F···F interaction (compliance constant: 6.96 Å/mdyn) leads to a marked intrinsic flexibility around the central C–C bond.

X-ray Diffraction Study of 1Z

The molecule (Figure 3) exhibits crystallographic twofold symmetry. The fluorine substituent is slightly disordered, but the minor component, which represents an alternative orientation of the (*Z*) isomer, is only 7% occupied; thus, any effects of disorder on the structure should be minimal. The intramolecular F···F distance is 2.638(2) Å and the torsion angles about the central bond C9–C9′ are 36.9(3)° for C9A and 38.6(3)° for C8A. The angle between the C–F vectors is 36.4°.

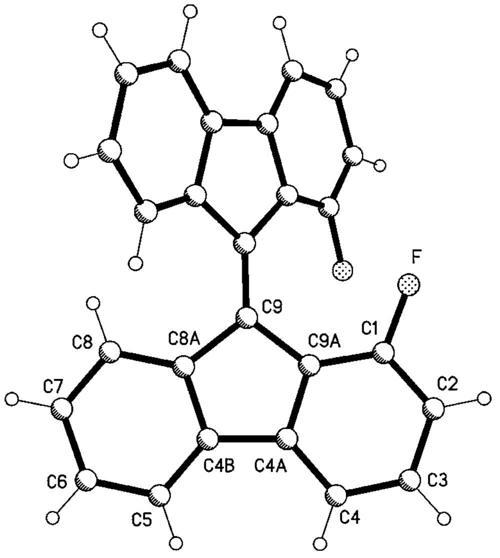


Figure 3. The molecule of **1Z** in the crystal. Radii are arbitrary. Only the asymmetric unit is numbered. The minor disorder component is omitted for clarity.

The molecular packing (Supporting Information, Figure S3) involves borderline intermolecular F···F contacts of 2.824(2) Å and, more significantly, C–H···π interactions from H2 to the centroid of C5–8,C8A,C4B with H···Cent 2.62 Å (normalized), angle 150°. The net effect is to form double layers of molecules parallel to the *yz* plane at $x \approx$ 0,1/2,1 etc.

Conclusions

Both from the X-ray diffraction study and from the B3LYP/6-31+G(d) calculation of **1Z** as an isolated molecule the torsional angle about the central C=C bond was found to be in the range 34–39°. The two C–F bonds form an angle of ca. 35° and the F···F distance is 2.64–2.71 Å. This geometry strongly deviates from the geometries of compounds **2**–**5**, where the C–F bonds are nearly parallel, and this correlates with the fact that the prediction of the through-space *J*(F,F) coupling constant in **1Z** by means of Equation (1) fails. The predicted value of ca. 46 Hz is much larger than the experimental value of 11.0 Hz. This and the similar finding for difluorometaparacyclophane **6** indicate that the size of F,F through-space coupling constants depends not only on the F,F distance but also on the angle between the C–F bonds. Further compounds of suitable geometry will have to be investigated to obtain a more detailed picture.

Experimental Section

General: The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400.1, 100.6 and 376.5 MHz, respectively, at room temperature (ca. 295 K). The chemical shifts are given with respect to the internal standards tetramethylsilane (^{1}H: δ = 0 ppm), CDCl$_3$ (^{13}C: δ = 77.0 ppm) and virtual CCl$_3$F (^{19}F: δ = 0 ppm), i.e. the CCl$_3$F frequency had been determined earlier from a solution of CCl$_3$F in CDCl$_3$ (ca. 1% by volume). The assignments of the ^{1}H and ^{13}C resonances were achieved by measuring 2D spectra (H,H-COSY, H,C-HSQC and H,C-HMBC) and by inspection of the F,H and F,C coupling constants. The ^{1}H NMR spectra of the mixture of **1E**/**1Z** and of the parent compound 9,9′-bifluorenylidene[26,27] were analyzed with the Bruker program Win-DAISY 4.05 by iterating on the full lineshape.

1,1′-Difluoro-9,9′-bifluorenylidene (1, Mixture of Stereoisomers): The product (0.22 g, 45%) was obtained from 9-bromo-1-fluorofluorene (0.71 g, 2.7 mmol) according to the reaction conditions given in ref.[15] Pentane/CH$_2$Cl$_2$ (12:5) was used for the chromatographic purification on neutral alumina instead of hexane/benzene (2:1); red needles, m.p. 208 °C (CH$_2$Cl$_2$) (ref.[15] 208 °C). For ^{1}H-, ^{13}C- and ^{19}F NMR spectroscopic data, see text. Iterative analysis[18] of the ^{1}H NMR spectrum showed the composition of the product to be 69:31 (**1Z**/**1E**).[28] By serendipity the crystal that was selected for the X-ray diffraction study contained only **1Z**, the (*Z*) isomer of **1**.

9,9′-Bifluorenylidene:[26,27] Prepared from 9-bromofluorene under the reaction conditions given for the preparation of **1** in ref.[15] ^{1}H NMR (CDCl$_3$): δ = 7.205 (m, 4 H, 2,7-H), 7.325 (m, 4 H, 3,6-H), 7.699 (m, 4 H, 4,5-H), 8.380 (m, 4 H, 1,8-H) ppm; $J(1,2)$ = 7.93, $J(1,3)$ = 0.97, $J(1,4)$ = 0.67, $J(2,3)$ = 7.35, $J(2,4)$ = 1.17, $J(3,4)$ = 7.58 Hz; *R* factor of the iteration = 0.18%. ^{13}C NMR (CDCl$_3$): δ = 119.9 (CH, 4 C, C-4,5), 126.7 (CH, 4 C, C-1,8), 126.8 (CH, 4 C, C-2,7), 129.1 (CH, 4 C, C-3,6), 138.3 (C$_q$, 4 C, C-8a,9a), 141.0 (C$_q$, 2 C, C-9), 141.3 (C$_q$, 4 C, C-4a,4b) ppm.

X-ray Structure Determination of 1Z: Crystal data: C$_{26}$H$_{14}$F$_2$ (364.39), monoclinic, space group *C*2/*c*, a = 22.597(4), b = 7.8877(14), c = 9.664(2) Å, β = 104.261(6)°, V = 1669.4 Å^3, Z = 4, μ(Mo-K_α) = 0.10 mm^{-1}, T = –140 °C. Data collection: A red tablet (ca. 0.4 × 0.4 × 0.2 mm) was used to record 6346 intensities with a Bruker SMART 1000 CCD diffractometer (Mo-K_α radiation, $2\theta_{max}$ = 60°). Structure refinement: The structure was refined anisotropically on F^2 (program SHELXL-97: G. M. Sheldrick, Univ. of Göttingen) to wR_2 = 0.145, R_1 = 0.054 for 132 parameters and 2394 unique reflections; S = 1.07, max. $\Delta\rho$ = 0.6 e·Å^{-3}. The hydrogen atoms were included using a riding model. Special feature of refinement: The fluorine atom is slightly disordered; the alternative site (at C8 rather than C1) is, however, occupied to the extent of only 7%. The C–F bond lengths of both components were restrained equal. CCDC-229812 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental and theoretical ^{1}H NMR spectrum (obtained by iterative analysis) of the **1Z**/**1E** mixture (Figure S1), ^{13}C satellites in the ^{19}F NMR spectrum of **1Z** including spectra calculated for the two solutions of the ABX system (Figure S2), molecular packing diagram of **1Z** (Figure S3).

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[1] Chemical parlance knows the “bay” region in phenanthrene, which has three sides, and the “fjord” region (four sides) in benzo[*c*]phenanthrene. There does not seem to exist a catchy term for the inner region in [5]helicene (five sides) or in the related compounds **1** or 9,9′-bifluorenylidene of this paper. We suggest to call it a “cove”, which is “a circular or round inlet with a narrow entrance” (http://en.wikipedia.org/wiki/Cove as of March 18, 2005). This term would be most apt if the compounds in question were planar.

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[28] A referee suggested to attempt a separation of **1E** and **1Z**. This can be achieved by means of reversed-phase HPLC [conditions: LiChroCART 250-4 column with Purospher STAR RP-18e, 5 µm, CH_3CN/H_2O (60:40, isocratic), 0.7 mL/min, 52 bar, DAD detector, λ = 350 nm; t_R = 15.9 min (**1E**) and 16.9 min (**1Z**)]. We are grateful to Dipl.-Chem. Madalina Stefan for carrying out the HPLC experiments.

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