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Communications to the Editor

Through-Bond and Through-Space J_{FF} Spin−Spin Coupling in Peridifluoronaphthalenes: Accurate DFT Evaluation of the Four Contributions

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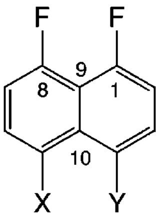
Fluorine−fluorine NMR spin−spin coupling constants (J_{FF}) have become powerful probes for structural analysis of molecules in the fields of chemistry and biology.[1] Unusually large couplings between fluorine atoms connected by more than three chemical bonds have been characterized as "through-space", T−S, couplings.[2] The latter exhibit a dependence on the distance d_{FF} between the coupled atoms.[3] A limited but quantitative exponential correlation between d_{FF} and $J_{FF}{}^{T-S}$ has been proposed by Ernst and Ibrom based on a series of molecules in which the fluorine atoms are separated by 7−8 bonds.[4] In a more recent paper, Mallory and colleagues examined the d_{FF} distance dependence of J_{FF} for a series of 18 substituted 1,8-difluoronaphthalenes **1** in which the fluorine atoms are removed by only four bonds.[5] They likewise derived a satisfying exponential correlation of d_{FF} and J_{FF} similar to that reported by Ernst and Ibrom and concluded that exclusive through-space interactions explain it. Importantly, five of the 1,8-difluoronaphthalenes do not fit the correlation and were excluded from it. These deviations and their underlying source are the subject of this communication. We present our efforts to calculate explicitly the four terms contributing to J_{FF} (Fermi contact (FC), spin dipolar (SD), paramagnetic spin−orbit (PSO), and diamagnetic spin−orbit (DSO)) and conclude that analogues of **1** are subject to both through-bond (T−B) and through-space (T−S) fluorine−fluorine coupling.



	X	Y
1a	H	H
1b	Me	Me
1c	-CH$_2$-CH$_2$-	
1d	-CH=CH-	

To investigate the d_{FF}/J_{FF} conundrum, we began by optimizing the molecular geometries of **1a−d**[6] at the DFT-B3LYP/6-311G** level with Gaussian 98.[7] All four components of the F−F spin−spin couplings were calculated at the DFT-B3LYP level of theory by using a modified version of Gaussian-98.[8−10] The B3LYP functional was employed since it has been reported to provide reliable *J*-coupling predictions.[11] In addition, all J_{FF} calculations were performed with a partially enriched, correlation-consistent basis set composed of cc-pVDZ[12] for carbon and hydrogen and aug-cc-pCVDZ[12] for fluorine, a medium-sized basis set known to deliver accurate values for J_{FF} couplings.[13] As a practical matter, FC[8] and SD[9] terms were evaluated by means of finite perturbation theory (FPT), while the PSO contribution was obtained via coupled perturbed DFT theory (CPDFT). Since Gaussian-98 does not presently calculate one-electron integrals for the PSO and DSO components, these were determined with the DALTON 1.0 package.[14] The calculated total couplings for **1a−d** (Table 1) are in good agreement with experiment. FC is the largest term in all cases, although in **1d** the sum of non-contact terms is larger than FC. As shown previously, this term increases nonlinearly with decreasing distance d_{FF}.[15] It is noteworthy that the DSO contributions in Table 1 are small for all four compounds. Although the PSO and SD terms are likewise diminutive for **1a−c**, they have risen significantly for the structure **1d**.

Recently, Arnold et al.[16] computed a series of DFT-based J_{FF} couplings and the corresponding FC, PSO, and DSO terms for

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Table 1. Calculated J_{FF} Coupling Constants[a] (Hz) and Optimized[b] d_{FF} Distances (Å) for Substituted Peridifluoronaphthalenes **1a**−**d**

	1a	**1b**	**1c**	**1d**
FC[c]	50.5	88.6	25.5	21.3
SD[c]	0.2	0.8	−1.4	3.7
PSO[d]	4.7	0.0	4.6	18.5
DSO	1.0	1.1	0.9	0.8
total	56.4	90.5	29.6	44.3
exptl[e]	59.0	85.2	28.4	36.7
d_{FF}[b]	2.622	2.493	2.753	2.78

[a] Obtained with the B3LYP functional and the basis set aug-cc-pCVDZ for F and cc-pVDZ for C and H. [b] Full geometry optimizations were performed at the B3LYP/6-311G** level. [c] Numerical energy derivatives with FPT. [d] Analytical energy derivatives with CPDFT. [e] Experimental values were taken from ref 5.

truncated models of peridifluoronaphthalenes lacking all or most of the naphthalene ring and devoid of substituents X and Y. The SD contribution was regarded as negligible and therefore neglected. The calculations reproduce the exponential trends in most cases, but they do not explain the J_{FF} behavior of **1d** and the other anomalous analogues, nor do they comment on the possibility for simultaneous through-space and through-bond transmission. An interesting feature of the work is that the PSO term exhibits a negative contribution to the total coupling in T−S models as determined empirically[3c,d] and a positive one when both T−S and T−B mechanisms have the capacity to work together in the same molecule. The dichotomy can be understood as competition between a negative T−S and a positive T−B transmission in J_{FF}. Thus, the large and positive PSO term for **1d** (Table 1) can be interpreted as being dominated by the T−B mechanism, causing its deviation from the $d_{\mathrm{FF}}/J_{\mathrm{FF}}^{\mathrm{T-S}}$ exponential curve. To test this assertion, the F- - -F distance in **1d** was adjusted by varying the C−C−F bond angle slightly so that d_{FF} is equal to that in optimized **1c**. Calculation of the PSO term for the modified **1d** structure causes $J_{\mathrm{FF}}^{\mathrm{PSO}}$ to inflate from 18.5 to 19.2 Hz. In parallel, calculation of the PSO term for the HF- - -FH dimer was performed at the same level with **1c**/**1d** F- - -F distances of 2.750 and 2.780 Å to obtain −25.0 and −23.3 Hz, respectively. These last couplings are transmitted totally T−S, and, as expected, $J_{\mathrm{FF}}^{\mathrm{PSO}}$ increases in absolute value with decreasing F- - -F distance. By contrast, for **1d** the same term increases positively with decreasing d_{FF}, suggesting an overriding T−B transmission mechanism.

A second measure of relative T−B vs T−S coupling focuses exclusively on the Fermi contact term, the largest J_{FF} contributor for compounds **1a**−**d**. To the latter, we have applied natural *J*-coupling analysis (NJC)[15] based on Weinhold et al.'s Natural Bond Orbital (NBO) localization treatment,[17] a procedure that partitions the FC term into contributions from localized lone pair, bond, and core orbitals (Table 2). As shown previously,[15] the FC term is transmitted mostly T−S by the positive and large contributions of fluorine lone pairs, LP(F), and fluorine core orbitals, CR(F). However, as illustrated by Table 2, the C−C and C−H bonds of the aromatic rings in **1** likewise make a substantial T−B contribution (10−20% in **1a**−**c**). The five C−C bonds in question include those flanking C1 and C8 as well as the C9−C10 bond. Furthermore, the C−F bonds undoubtedly add to the T−B sum, although separation of T−B and T−S constituents is not possible with NJC. It is noteworthy that the C−X (X = H, C, F) $J_{\mathrm{FF}}^{\mathrm{T-B}}$ components are not constant across the **1a**−**d** series. In particular, **1d** displays a quantitatively different partition of T−B coupling contributions that highlight its anomolous *J*-coupling properties.

Table 2. NJC[a] Dissection of the FC Term for Substituted Peridifluoronaphthalenes **1a**−**d** (Hz)

	1a	**1b**	**1c**	**1d**
LP(F)[b]	53.7	116.5	31.1	22.2
CR(F)[c]	7.0	15.3	3.4	0.7
C−F[d]	0.2	−31.4	−0.7	−0.1
C−C[e]	−11.0	−11.9	−8.1	−1.4
C−H[f]	0.6	0.1	−0.2	−0.1

[a] NJC analysis was performed as in ref 15. [b] Obtained as the sum of both fluorine lone pair contributions. [c] Sum of all fluorine core contributions. [d] Sum of both C−F bond contributions. [e] Sum of all C−C bond contributions. [f] Sum of C−H bond contributions.

In conclusion, by a judicious choice of methodology and basis sets, we have been able to calculate J_{FF} reasonably accurately for the full geometries of a set of 1,8-difluoronaphthalenes spanning a 57 Hz empirical range (Table 1) along with the underlying FC, SD, DSO, and PSO terms. The PSO and **1d**-SD factors make a sizable contribution to the total four-bond F−F coupling constant. Importantly, both the FC and PSO terms are strongly suggested to incorporate significant through-bond (T−B) components that are unevenly distributed across structures such as **1a** and **1d**. The same has been deduced for the SD term associated with a four-bond C−F coupling when strong π-conjugation intervenes between the coupled centers[9] as it does in the present cases. The inability of the exponential $d_{\mathrm{FF}}/J_{\mathrm{FF}}^{\mathrm{T-S}}$ correlation to accommodate **1d** and similar structures is thereby illuminated. In these cases the experimental J_{FF} deviations amount to 5−13 Hz.[5] Variations in the magnitude of the various underlying terms and the estimated extent of T−B coupling are more than sufficient to account for them. We anticipate that attempts to unify the geometric dependence of F−F coupling constants across a broader range of difluorinated structures will fail owing its origin to the same phenomena. Likewise, other molecular systems that might otherwise appear to exhibit exclusive through-space coupling, but mask T−S and T−B blends, will be subject to the principles outlined here as pointed out recently by Bryce and Wasylishen.[13] Future work will attempt to unravel some of these complexities.

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