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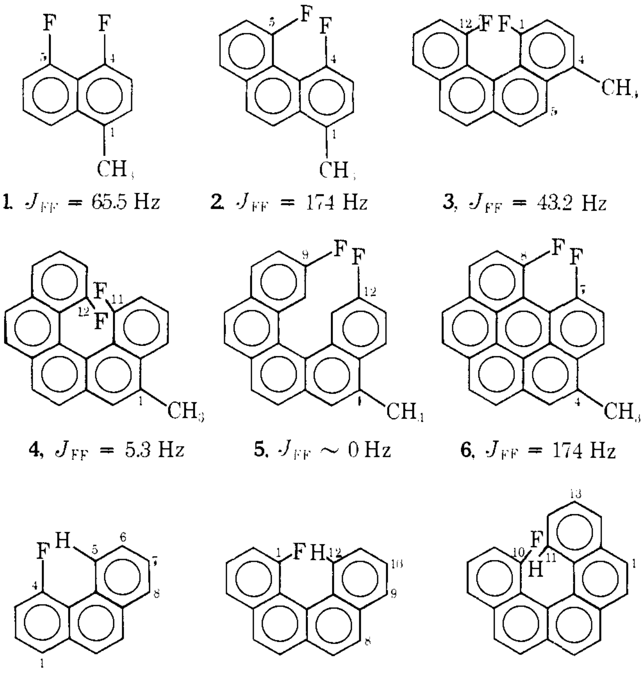
Nuclear Spin–Spin Coupling via Nonbonded Interactions. III. Effects of Molecular Structure on Through-Space Fluorine–Fluorine and Hydrogen–Fluorine Coupling[1]

Sir:

The concept[2] that certain intramolecularly crowded atoms can experience nuclear spin-spin coupling predominantly via through-space (or direct) nonbonded interactions of the two atoms, as opposed to interactions involving the intervening bonds, continues to receive considerable attention. Many examples have been reported for both FF[3,4] and HF[2a,5] coupling, and several theoretical treatments have appeared.[1a,6] Some initial findings of the systematic investigations we are undertaking of through-space coupling in polynuclear aromatic systems are presented in Chart I.[7,8]

The values of J_{FF} observed for **1–6**[9] support the idea that the magnitude of through-space FF coupling depends on the internuclear distance. For example, the FF distance in the difluorophenanthrene **2** obviously is shorter than that in the difluoronaphthalene **1**, which accounts for J_{FF} being much larger for **2** than for **1**. In the series of difluoro compounds **2–5**, the sharply decreasing values of J_{FF} (**2**, 174 Hz;[10] **3**, 43.2 Hz;[11] **4**, 5.3 Hz;[12] **5**, ca. 0 Hz) are consistent with the expectation that out-of-plane distortions in these helical molecules give rise to increasing FF distances in the sequence **2** < **3** < **4** < **5**. The observation of the same J_{FF} value of 174 Hz for both the benzo[*ghi*]perylene derivative **6**[12] and the phenanthrene derivative **2** reflects the similar spatial relationship of the two fluorines in these compounds.

Chart I. Through-space FF and HF coupling constants for compounds 1–9.



1, J_{FF} = 65.5 Hz
2, J_{FF} = 174 Hz
3, J_{FF} = 43.2 Hz
4, J_{FF} = 5.3 Hz
5, J_{FF} ~ 0 Hz
6, J_{FF} = 174 Hz
7, $J_{H\text{-}5,F}$ = 2.6 Hz
8, $J_{H\text{-}12,F}$ = 14.5 Hz
9, $J_{H\text{-}11,F}$ = 1.7 Hz

Coupling between bay hydrogen and fluorine nuclei in 4-fluorophenanthrenes has apparently not been reported previously. In addition to the value of 2.6 Hz[13] for the coupling between H-5 and F-4 in 4-fluorophenanthrene (**7**) itself, we find the following values of J_{54} for seven different substituted derivatives of **7**:[14] 8-methyl, 2.9 Hz; 8-chloro, 3.8 Hz; 6-fluoro, 3.8 Hz; 6-chloro, 4.4 Hz; 6-bromo, 4.4 Hz; 6-methoxy, 4.6 Hz; and 7-fluoro-1-methyl, 4.6 Hz. To our knowledge, the value of 14.5 Hz[12] for the coupling between H-12 and F-1 in 1-fluorobenzo[*c*]phenanthrene (**8**) exceeds in magnitude all previously reported values for through-space HF coupling via nonbonded interactions.[15] We also find the following values of $J_{12,1}$ for four different substituted derivatives of **8**:[7] 9-methoxy, 14.6 Hz; 9-bromo, 14.7 Hz; 9-cyano, 15.3 Hz; and 10-fluoro-8-methyl, 14.3 Hz. A value of 1.7 Hz is found for the coupling constant for H-11 and F-10 in 10-fluorodibenzo[*c,g*]phenanthrene (**9**) and also in its 13-fluoro-1-methyl derivative.

The patterns of our FF and HF coupling results show one striking and instructive feature as illustrated graphically in Figure 1: the magnitudes of the HF coupling constants in **7–9** run qualitatively parallel to those of the FF coupling constants in **1–3**, respectively, and there is no such parallelism for what might have been regarded as the structurally more comparable systems **7–9** and **2–4**, respectively. For example, the largest value of J_{FF} in the series **1–4** is found in the phenanthrene system **2**, whereas the largest value of J_{HF} in the series **7–9** is found not in the corresponding phenanthrene system **7** but rather in the benzo[c]phenanthrene system **8**. We believe this provides evidence for the concept that the nonbonded interactions of importance for through-space HF coupling are not those between F and H

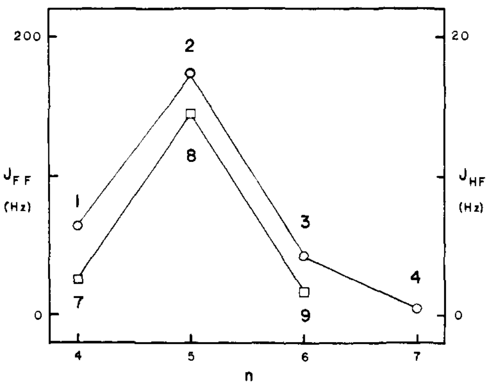


Figure 1. Values of J_{FF} (circles, left-hand ordinate) for compounds **1–4** and J_{HF} (squares, right-hand ordinate) for H-5, H-12, and H-11 in compounds **7–9**, respectively, plotted against *n*, where *n* is the number of bonds along the shortest pathway through the molecular framework that connects the two fluorines in **1–4** or that connects the fluorine and the *carbon* bearing the coupled hydrogen in **7–9**. The number of connecting bonds *n* is used here merely as an index of structural type in these polynuclear systems; coupling through these bonds is considered negligible in magnitude for all cases except **1** and **7**, in which small through-bond contributions to the observed coupling cannot be ruled out.

directly, since those interactions presumably would be optimized in **7** just as the FF interactions are evidently optimized in **2**, but rather are those between F and the *carbon* to which the H is attached.[16] Thus, we conclude that the large value of J_{HF} for the benzo[*c*]phenanthrene **8** results from an especially favorable spatial relationship between F-1 and C-12 in **8**, analogous to the especially favorable spatial relationship between F-4 and F-5 that gives rise to the large value of J_{FF} in the phenanthrene **2**.

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(7) Except as noted, values of J_{FF} and J_{HF} were determined from ^{19}F spectra at 56.4 MHz and ^1H spectra at 60 MHz in C_6D_6 solution.

(8) Full synthetic details for all new compounds will be reported later.

(9) Nomenclature: 1, 4,5-difluoro-1-methylnaphthene; **2**, 4,5-difluoro-1-methylphenanthrene; **3**, 1,12-difluoro-4-methylbenzo[*c*]phenanthrene; **4**, 10,11-difluoro-1-methyldibenzo[*c,g*]phenanthrene; **5**, 9,12-difluoro-1-methyldibenzo[*c,g*]phenanthrene; **6**, 7,8-difluoro-1-methylbenzo[*ghi*]-perylene.

(10) Values of 167–170 Hz have been reported previously for J_{FF} in several 1,8-disubstituted-4,5-difluorophenanthrenes by K. L. Servis and K.-N. Fang, *J. Am. Chem. Soc.*, **90**, 6712 (1968).

(11) The 5-methyl isomer of **3** has a J_{FF} value of 45.3 Hz.

(12) The ^{19}F spectra of **4** and **6** were measured in DMF at 94.1 MHz; the ^1H spectrum of **8** was measured in C_6D_6 at 100 MHz. We are grateful to Professor David R. Dalton of Temple University for obtaining these spectra.

(13) The signal for H-5 in the ^1H spectrum of **7** was simplified to a 2.6-Hz doublet (also 2.6 Hz in CCl_4) by decoupling all the other hydrogens.

(14) Measured in CCl_4 solution.

(15) Values of J_{HF} up to 16 Hz have been reported for the NH hydrogens in some 2-fluorobenzamide derivatives in which the nuclear spin information is thought to be transmitted through intramolecular HF hydrogen bonds.[5ll]

(16) This concept has been suggested previously on the basis of HF coupling studies involving aliphatic hydrogens.[5n,u,cc] See also ref 5ee.

(17) (a) This work is taken in part from the Ph.D. Thesis of W.M.R., Bryn Mawr College, 1974; (b) National Science Foundation Trainee, 1969–1970, and U.S. Steel Foundation Fellow, 1970–1972.

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Flash Pyrolysis of α-(*p*-Tolylsulfonyl)phenyldiazomethane. Carbene Formation by Loss of Sulfur Dioxide[1]

Sir:

This communication is prompted by our discovery of the apparent expulsion of sulfur dioxide from a sulfene. Such extrusion reactions were postulated over 60 years ago,[2] but no example has withstood close attention. As remarked in a recent cogent review,[3] loss of sulfur dioxide from a sufene is "conspicuously absent", and all earlier attempts to use external addition reactions to trap the carbene so formed have failed.[2,4-6] The Wolff-like rearrangement of sulfonyl carbenes to give sulfenes is known[7] and our interest in carbene chemistry and the use of gas-phase reactions of carbenes[8] in synthesis led us to examine the flash pyrolysis of α-(*p*-tolylsulfonyl)phenyldiazomethane (**1**).[9]

It was our thought that a carbene might be trapped more successfully by an internal reaction rather than an external addition, and we further hoped that the two benzene rings would render the fragmentation substantially less endothermic than the 55–60 kcal/mol estimated for the cleavage of