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Nuclear Spin–Spin Coupling via Nonbonded Interactions. 6. F–F Coupling through an Intervening Phenyl Group[1]

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Abstract: Evidence is presented for a novel type of "through-space" nuclear spin–spin coupling involving two fluorine atoms that are intramolecularly crowded against opposite sides of an intervening group X. The first example of this new phenomenon of F–X–F coupling involves the interaction of F-1 and F-8 through the intervening C-9 phenyl group in 1,5,8-trifluoro-9,10-diphenylanthracene (**1**) with a coupling constant of $J_{1,8}$ = 6.4 Hz. The "through-bond" component of this coupling is estimated as 1.1 Hz on the basis that $J_{1,8}$ = 1.1 Hz for 1,5,8-trifluoroanthracene (**2**). The fact that the magnitude of $J_{1,8}$ is significantly larger in **1** than in **2** is attributed to a novel coupling mechanism in **1** involving overlap interactions between the in-plane 2p lone-pair orbitals on the two fluorine atoms and the nearly isoenergetic lowest energy π molecular orbital on the C-9 phenyl group. To rationalize the small value of $J_{1,8}$ = 0.8 Hz for 1,5,8-trifluoroanthraquinone (**3**), it is argued that the in-plane 2p lone-pair orbital on the oxygen atom of the C-9 carbonyl group, which would be the relevant intervening orbital for F–X–F coupling, is much higher in energy than the fluorine in-plane 2p lone-pair orbitals, and this energy mismatch allows only a weak interaction between these two types of orbital.

It is well-known[3] that pairs of fluorine atoms that are intramolecularly crowded against one another can exhibit exceptionally large F–F nuclear spin–spin coupling constants, J_{FF}. Examples include various 1,8-difluoronaphthalenes (J_{FF} = 59–75 Hz)[4] and 4,5-difluorophenanthrenes (J_{FF} = 174 Hz).[5] This phenomenon of "through-space" F–F coupling has been attributed[6] to the generation of a pair of *two*-center molecular orbitals, one bonding and one antibonding, as a consequence of the spatial overlap of two nominally *one*-center 2p lone-pair orbitals as illustrated schematically in Figure 1.

As a corollary of this theory that through-space F–F coupling depends on the overlap of lone-pair orbitals, we predicted earlier that molecules with suitably oriented ^{15}N and ^{19}F atoms should exhibit through-space N–F coupling. The successful experimental verification of that prediction was reported in part 5 of this series.[1a]

We also have used this lone-pair orbital overlap theory to predict the existence of a previously unobserved type of intramolecular spin–spin coupling between fluorine nuclei in which the two fluorine atoms are not crowded directly against one another, but rather are both crowded in a nonbonded way against opposite sides of an intervening group X that bears a p-type lone-pair orbital (or a filled π orbital) oriented such that one lobe of this X orbital overlaps with a 2p lone-pair orbital on one of the fluorine atoms and the other lobe of this X orbital overlaps with a 2p lone-pair orbital on the other fluorine atom. The overlap interactions of these *three* basis atomic orbitals would give rise to a set of *three* molecular orbitals, consisting of one bonding orbital, one nonbonding orbital, and one antibonding orbital. We reasoned that although the six electrons occupying these three molecular orbitals would not provide any net chemical bonding, they should transmit nuclear spin information between the two fluorine nuclei. We now report what we believe is the first example that confirms our theoretical prediction of this novel F–X–F coupling.

Scheme I

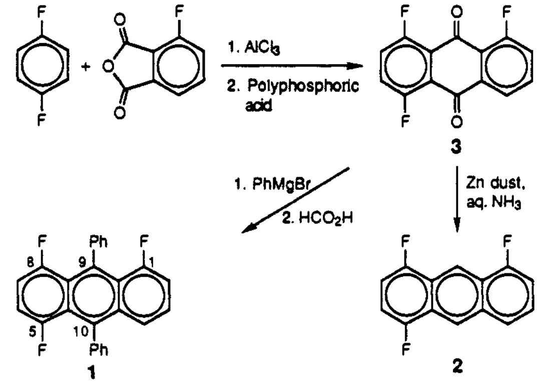

Table I. NMR F–F Coupling Constants (Hz)

compd	$J_{1,8}$	$J_{1,5}$	$J_{5,8}$
1	6.4	1.3	23.0
2	1.1	1.1	22.8
3	0.8	≤0.4	18.1

Results and Discussion

For our first scouting experiment, we chose to compare the coupling between F-1 and F-8 in 1,5,8-trifluoro-9,10-diphenyl-

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(1) (a) Part 5: Mallory, F. B.; Mallory, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 4816. (b) Presented in part at the 188th National Meeting of the American Chemical Society, Philadelphia, PA, August 27, 1984; ORGN-68.

(2) (a) Bryn Mawr College. (b) University of Pennsylvania.

(3) See earlier parts in this series and references cited therein.

(4) Mallory, F. B.; Mallory, C. W.; Fedarko, M. *J. Am. Chem. Soc.* **1974**, *96*, 3536.

(5) Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 4770.

(6) (a) Mallory, F. B. *J. Am. Chem. Soc.* **1973**, *95*, 7747. (b) Numerous other theoretical formulations have been suggested, as described in references cited by: Schaefer, T.; Marat, K.; Lemire, A.; Janzen, A. F. *Org. Magn. Reson.* **1982**, *18*, 90.

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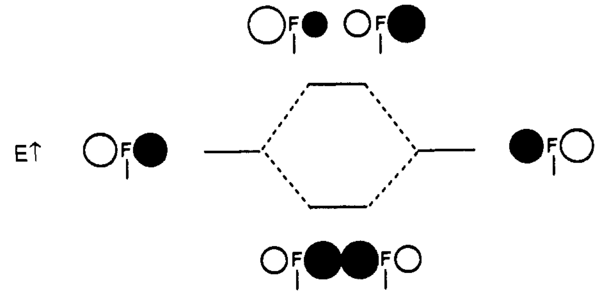


Figure 1. Illustration of the overlap interactions of two 2p lone-pair basis atomic orbitals that generate the filled bonding and antibonding molecular orbitals thought to be involved in through-space F–F coupling.

anthracene (**1**) with the coupling between F-1 and F-8 in the corresponding compound lacking the phenyl groups, 1,5,8-trifluoroanthracene (**2**). Samples of both of these previously unknown compounds were prepared by way of 1,5,8-trifluoroanthraquinone (**3**) as a key synthetic intermediate, as illustrated in Scheme I.[7]

The coupling constants given in Table I were obtained from ^{19}F NMR spectra of compounds **1**–**3** measured at 282.4 MHz with complete ^1H decoupling. For the reference compound **2**, the results show that F-1 is coupled weakly to F-8, presumably by a through-bond interaction over a six-bond pathway; the magnitude of the measured coupling constant is $J_{1,8} = 1.1$ Hz. Gratifyingly, the ^{19}F NMR spectrum of the phenyl-substituted compound **1** shows that the coupling constant $J_{1,8}$ has the significantly larger magnitude of 6.4 Hz! If it is assumed that the magnitude of the through-bond contribution to $J_{1,8}$ in **1** is equal to the magnitude of the observed $J_{1,8}$ coupling in **2**, then the magnitude of the contribution of the novel F–X–F coupling in **1** through the intervening C-9 phenyl group can be evaluated as either 6.4 Hz − 1.1 Hz = 5.3 Hz or 6.4 Hz + 1.1 Hz = 7.5 Hz, depending on whether the through-space and through-bond components have the same or the opposite signs, respectively.

An X-ray crystallographic analysis[8] of **1** demonstrates that the two phenyl groups are oriented with their ring planes essentially perpendicular[8] to the plane of the anthracene ring and also shows that F-1 and F-8 each are separated by ~2.6 Å from the C-1′ carbon atom of the phenyl group that is attached to C-9. This carbon–fluorine separation is ~0.5 Å less than the sum of the van der Waals radius of fluorine (1.4 Å) and the van der Waals half-thickness of a phenyl group (1.7 Å).

As indicated in Table I, the magnitude of the coupling between F-1 and F-8 in quinone **3** is only 0.8 Hz. In order to judge the extent to which this observed coupling might represent F–X–F coupling through the intervening carbonyl group, an estimate of the magnitude of the through-bond contribution to this coupling would be required. The following argument represents one attempt to make this estimate. Because the CC bonds linking C-9 to the flanking aromatic rings in quinone **3** have smaller π bond orders than the corresponding bonds in anthracene **2**, one might expect that the magnitude of the through-bond component of $J_{1,8}$ in **3** would be smaller than the value of 1.1 Hz found (Table I) for $J_{1,8}$ in **2**. (Consistent with this notion, the magnitude of the coupling of F-1 and F-5 in these two systems, which occurs only by through-bond interactions, is smaller in **3** (≤ 0.4 Hz) than in **2** (1.1 Hz), as shown in Table I.) Assuming that the upper limit for the magnitude of the through-bond component of $J_{1,8}$ in quinone **3** is 1.1 Hz (as in **2**), and given the observed magnitude of 0.8 Hz for the total $J_{1,8}$ coupling in **3**, one can show that the through-space component of $J_{1,8}$ in **3** lies between 0.0 and 0.8 Hz if the two components have the same sign and lies either between 0.0 and 0.3 Hz or between 0.8 and 1.9 Hz if the two components have opposite signs. In any event, the intervening carbonyl group in **3** evidently is much less effective than the intervening phenyl group in **1** at transmitting F–X–F coupling, as shown by the fact that the magnitude of F–X–F coupling in **3**, with a value lying somewhere in the range of 0.0–1.9 Hz, is considerably smaller than the magnitude of either 5.3 or 7.5 Hz that we have established as discussed above for the F–X–F coupling in 1.

Scheme II

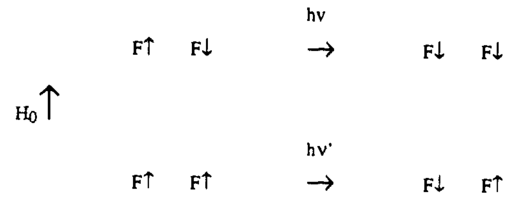
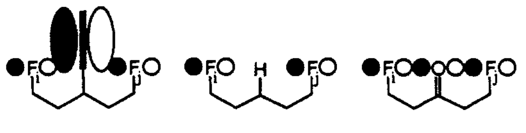


Chart I



4a **4b** **4c**

Theoretical Interpretation

The theoretical treatment presented here to account for this new phenomenon of through-space F–X–F coupling by *indirect* nonbonded interactions through an intervening filled orbital is fundamentally the same as that employed earlier[6a] to rationalize through-space F–F coupling by *direct* nonbonded interactions between two fluorine atoms.

For any pair of fluorine atoms in a rapidly tumbling molecule in a large and constant external magnetic field H_0, the magnitude of the nuclear spin–spin coupling constant J_{FF} measures the degree to which the energy of the photon (typically in the radio-frequency range) that is required to flip the spin of one of the fluorine nuclei (from the alignment "with" H_0 to the alignment "against" H_0) depends on the spin state ("with" or "against" H_0) of the other fluorine nucleus. In terms of the formulation presented in Scheme II, J_{FF} is proportional to the difference in the two transition energies, $h\nu - h\nu'$.

Finite values of J_{FF} arise because electrons in the immediate vicinities of the fluorine nuclei experience spin polarization: that is, under the perturbation of the two nuclear spins, the electrons with α spin adopt a spatial distribution of electron density that is slightly different from that adopted by the electrons with β spin. The magnitude of the energy difference $h\nu - h\nu'$ depends on the degree to which molecules with *antiparallel* spins of their two fluorine nuclei have either an energetically more favorable ($h\nu - h\nu' > 0$ and $J_{FF} > 0$) or an energetically less favorable ($h\nu - h\nu' < 0$ and $J_{FF} < 0$) distribution of electron spin density as compared to molecules with *parallel* spins of their two fluorine nuclei. Two types of interaction are important in this context: Fermi contact interactions between electron spins and nuclear spins, and Hund interactions between pairs of electron spins.[6a] For our present purposes, it is not necessary to discuss in detail how these two types of spin–spin interactions occur or to know for a particular molecule whether it is the antiparallel or the parallel nuclear spin arrangement that permits the energetically more favorable summation of Fermi and Hund interactions. It suffices merely to note that nuclear spin–spin coupling requires the existence of nonzero electron spin densities in the immediate vicinities of each of the two coupled fluorine nuclei.

In the following presentation, our orbital overlap theory for through-space coupling between the nuclei of two fluorine atoms, F_i and F_j, is applied to intramolecular arrays of the general structural types of **4a**, **4b**, and **4c** shown in Chart I. The central sp^2 carbon atom of the planar framework bears a phenyl group oriented with its plane perpendicular to the plane of the framework

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[7] The numbering scheme employed here for compounds 1, 2, and 3 is convenient in the context of the present discussion. The correct names are as follows: 1 is 1,4,5-trifluoro-9,10-diphenylanthracene, 2 is 1,4,5-trifluoroanthracene, and 3 is 1,4,5-trifluoroanthraquinone.

[8] This analysis was carried out by Dr. Patrick J. Carroll at the X-ray facility in the Department of Chemistry of the University of Pennsylvania. There are two inequivalent molecules in the unit cell. In one of these molecules, the dihedral angle between the plane of each phenyl group and the plane of the anthracene ring is 88.8 (2)°; in the other molecule this dihedral angle is 84.6 (2)°.

Chart II

$n_S = n_i + n_j$ $n_A = n_i - n_j$

Chart III

(a)	F_i {n_S (α), n_A (β)}	F_j {n_S (β), n_A (α)}
(b)	F_i {n_S (β), n_A (α)}	F_j {n_S (α), n_A (β)}
(c)	F_i {n_S (α,β)}	F_j {n_A (α,β)}
(d)	F_i {n_A (α,β)}	F_j {n_S (α,β)}

in **4a**, bears a hydrogen atom in **4b**, and is part of a carbonyl group in **4c**.

For this discussion, the relevant basis atomic orbitals for the two fluorine atoms are the in-plane 2p lone-pair orbitals n_i (on atom F_i) and n_j (on atom F_j).[9] Given the symmetry of arrays **4a–c**, a proper starting point for the orbital description of these systems employs the symmetry-adapted basis orbitals n_S and n_A, which can be written (ignoring normalization factors for simplicity) as the symmetric and antisymmetric linear combinations, respectively, of the atomic orbitals n_i and n_j as shown in Chart II.

We believe (see below) that the pertinent basis orbital on the intervening phenyl group in **4a** is the lowest energy π orbital of that group. For the reference system **4b**, we assume for two reasons that there is no basis orbital on the central hydrogen atom capable of effective interaction with the n_i and n_j orbitals: (1) the σ and σ^* orbitals associated with the CH bond on the central carbon are too low and too high in energy, respectively, for significant mixing with these fluorine-based orbitals, and (2) there is minimal spatial overlap of these hydrogen-based and fluorine-based orbitals because the H and F atoms in this system are just barely in van der Waals contact with one another (the H–F distance in **4b** is ~2.5 Å compared with the sum of van der Waals radii of about 1.4 Å + 1.1 Å = 2.5 Å). In **4c**, the intervening basis orbital of interest is the in-plane 2p lone-pair orbital on the carbonyl oxygen atom.

For the simplest system, **4b**, we assume that the distance between F_i and F_j is sufficiently long (~5 Å) that there is no significant overlap between the n_i and n_j orbitals. Because of this lack of overlap, the symmetry-adapted wave functions n_S and n_A shown in Chart II would have *identical* space parts in the vicinity of each of the fluorine nuclei; that is, both n_S and n_A would look exactly like n_i in the vicinity of F_i, and both n_S and n_A would look exactly like n_j in the vicinity of F_j. Under these limiting circumstances, the Pauli principle[10] imposes strict demands on the spatial distribution of the four electrons in orbitals n_S and n_A: there can be no more than two electrons around each fluorine, and these two electrons must have opposed spins. Specifically, during an instant of time when the electron with α spin in the n_S orbital is close to the F_i nucleus, the electron with α spin in the n_A orbital is disallowed from being in the same region and, therefore, must instead be close to the F_j nucleus. The only allowed instantaneous electron configurations would be those illustrated in Chart III.[11] Thus, the n_S and n_A orbitals in a system like **4b** with no overlap between the basis orbitals n_i and n_j cannot sustain any net electron spin density around either fluorine atom, and therefore the four electrons in these two orbitals cannot contribute to F–F nuclear spin–spin coupling.

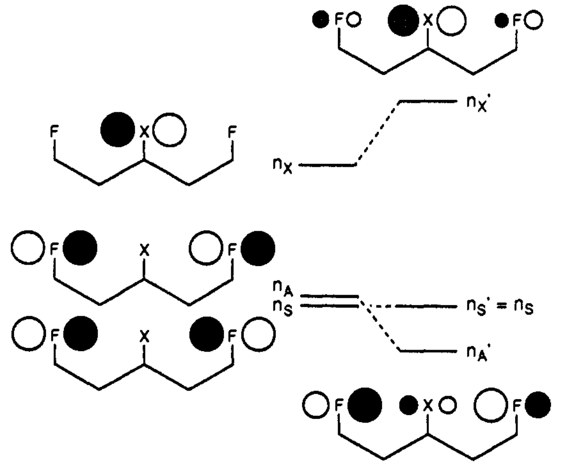

Figure 2. Illustration of the overlap interactions of three symmetry-adapted basis atomic orbitals (n_A, n_S, and n_X) that generate the filled bonding, nonbonding, and antibonding molecular orbitals (n_A', n_S', and n_X') thought to be involved in through-space F–X–F coupling. As a first approximation, $n_A' = n_A + \lambda n_X$, $n_S' = n_S$, and $n_X' = n_X - \lambda n_A$, where λ is a constant ($\lambda < 1$).

Chart IV

(a)	F_i {n_S' (α), n_A' (β)}	F_j {n_S' (β), n_A' (α)}
(b)	F_i {n_S' (β), n_A' (α)}	F_j {n_S' (α), n_A' (β)}
(c)	F_i {n_S' (α,β)}	F_j {n_A' (α,β)}
(d)	F_i {n_A' (α,β)}	F_j {n_S' (α,β)}
(e)	F_i {n_S' (α), n_A' (α)}	F_j {n_S' (β), n_A' (β)}
(f)	F_i {n_S' (β), n_A' (β)}	F_j {n_S' (α), n_A' (α)}

If it were possible, however, to perturb a system like **4b** in such a way that the orbitals of the n_S and n_A types would become differentiated from one another spatially in the vicinity of the fluorine nuclei, then the Pauli principle would not have the prohibitive effect described above. Depending on the extent of this spatial differentiation between the perturbed versions of the two orbitals, n_S' and n_A', there would be a finite probability for the existence of instantaneous electron configurations of types VIe and VIf indicated in Chart IV, in which the n_S' and n_A' electrons of the *same* spin would be located simultaneously in the immediate vicinity of the *same* fluorine nucleus.[12] (These VIe and VIf configurations would exist *in addition to* those of types VIa–d shown in Chart IV.)[11] Having configurations VIe and VIf available to be included in the weighted time-average that gives rise to the time-independent net spin density distribution in the molecule would contribute to a *positive* value of the nuclear spin–spin coupling constant J_{FF}. Thus, a molecule having *antiparallel* nuclear spins F_i and F_j would experience net Fermi contact interaction during that fraction of time that the molecule would possess the *antiparallel* distribution of electron spin density present in configurations VIe and VIf (i.e., a net excess of α electron spin density near one fluorine nucleus and a corresponding net excess of β electron spin density near the other fluorine nucleus). In one of these two configurations, the Fermi contact interaction would be *stabilizing* at both nuclei, and in the other of these two configurations, it would be *destabilizing* at both nuclei.[13] The

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[9] We have adopted the view that the valence-level orbitals on the fluorine atoms in our systems consist of two unhybridized lone-pair orbitals, $2p_y$ and $2p_z$ (with axes perpendicular to the CF bond axis), a lower energy lone-pair orbital that is mostly 2s with a slight admixture of $2p_x$, and a σ_{CF} bonding orbital that involves mostly $2p_x$ with a slight admixture of 2s. Our approach to the theoretical formulation of through-space F–F and F–X–F coupling would not be altered fundamentally by the assumption of some other hybridization scheme for fluorine.

[10] According to the Pauli principle, the wave functions for any two electrons in a molecule cannot be identical in *both* their space parts *and* their spin parts; thus, different spin parts are required if the two space parts are the same, but the same spin parts are permitted if the two space parts are different.

[11] We are excluding from consideration all instantaneous configurations with more than two electrons around one fluorine and fewer than two electrons around the other fluorine because such configurations are unreasonable energetically.

[12] It has been hypothesized[6a] that the magnitude of the net electron spin density that would exist around each fluorine atom in this type of situation, and hence the magnitude of the coupling constant J_{FF}, would depend on the degree of spatial dissimilarity of the n_S' and n_A' orbitals.

molecule would therefore experience a Boltzmann-type bias in the probability of the two configurations, with the energetically more favorable combination of nuclear and electron spins having a larger probability than the energetically less favorable combination of nuclear and electron spins. This would result in an overall net stabilization of the molecules with antiparallel nuclear spins. In contrast, a molecule having *parallel* spins of the F_i and F_j nuclei would experience no net Fermi contact stabilization through any of the instantaneous electron configurations in Chart IV.

One can imagine two ways in which the perturbation discussed in the preceding paragraph might be achieved. If the two fluorine atoms were sufficiently close together, they could experience direct overlap interactions between the n_i and n_j atomic orbitals, thereby generating a pair of spatially dissimilar bonding and antibonding two-center molecular orbitals. This is our view[6a] of the basis of the well-known through-space F–F coupling (Figure 1). Alternatively, if the two fluorine atoms were sufficiently crowded against an intervening group X bearing a suitably oriented filled p (or π) orbital, the nonbonded overlap interactions with that p (or π) orbital could render the n_S and n_A orbitals spatially different because the intervening orbital would be allowed by symmetry to interact only with n_A and not with n_S. This is our view of the basis of the novel through-space F–X–F coupling, as illustrated schematically in Figure 2 for the case of an intervening p orbital, n_X. (We would give a closely analogous theoretical treatment for the case of an intervening π orbital π_X.)

For interactions of the type shown in Figure 1, the two fluorine 2p basis orbitals have the same energy, and therefore, overlap of these orbitals is maximally effective in mixing them to generate two-center bonding and antibonding orbitals with different spatial distributions of electron density. For interactions of the type shown in Figure 2, however, the effectiveness of orbital mixing of basis orbitals n_A and n_X depends not only on their spatial overlap but also on how closely they are matched in energy. We suggest that orbital energy considerations can account for our experimental observation that much larger F–X–F coupling is found through the intervening phenyl group in anthracene **1** than through the intervening carbonyl group in anthraquinone **3**. As confirmed by preliminary ab initio molecular orbital calculations on model compounds,[14] the in-plane 2p lone-pair orbital on the carbonyl oxygen atom lies much higher in energy than the in-plane 2p lone-pair orbitals on the fluorine atoms (at ~–9.7 eV compared with ~–12.6 eV) in a system of type **4c**. As a consequence, even though this oxygen-based 2p orbital has both the correct symmetry and the needed spatial proximity to overlap with the fluorine-based antisymmetric n_A orbital, the magnitude of this interaction is small; according to the calculations,[14] the resulting n_S' and n_A' orbitals in a structure of type **4c** remain nearly degenerate, with an energy separation of only 0.1 eV. In contrast, the lowest energy π molecular orbital on the phenyl group[15] in a system of type **4a** is calculated[14] to lie quite close in energy to the 2p lone-pair orbitals on the fluorine atoms (at ~–12.4 eV compared with ~–12.6 eV). These calculations indicate that this phenyl orbital and the fluorine-based antisymmetric n_A orbital interact significantly to produce two antisymmetric mixed orbitals of the general types shown in Figure 2, thereby removing the degeneracy that would otherwise characterize the unperturbed n_S and n_A orbitals (the resulting n_A' orbital is calculated to lie ~1.0 eV below the n_S' orbital) and providing the spatial differentiation between these two orbitals that we believe is essential for F–X–F coupling in such a system.

Experimental Section

General Procedures. Melting points were measured with a Thomas-Hoover oil-bath apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. ^1H and ^{19}F NMR spectra were obtained in $CDCl_3$ solution at 17 °C, either with an IBM AF-NR300 spectrometer operating at 300.1 MHz for ^1H and 282.4 MHz for ^{19}F or with an IBM WP-200 SY spectrometer operating at 200.1 MHz for ^1H and 188.3 MHz for ^{19}F. Chemical shifts were measured in ppm downfield from Me_4Si for ^1H and in ppm downfield from 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane for ^{19}F. We estimate that our reported values for chemical shifts and coupling constants are reliable within ~0.005 ppm and ~0.2 Hz, respectively. Mass spectra were determined with a Hewlett-Packard 5890/5970 GC/MS system, a Hitachi Perkin-Elmer RMH-2 instrument, or a VG Micromass 70-70 double-focusing spectrometer. Sublimations at reduced pressure were carried out as described previously.[16]

3-Fluorophthalic Anhydride. Commercially available 3-fluorophthalic acid (25 g, 140 mmol) was heated slowly to 200 °C under reduced pressure (water aspirator). The residual solid was purified by sublimation at 140 °C and 0.002 Torr and by recrystallization from toluene to give 16 g (71%) of 3-fluorophthalic anhydride, mp 159.2–160.0 °C (lit.[17] mp 160 °C).

1,5,8-Trifluoro-9,10-anthraquinone (3). A mixture of 5.9 g (36 mmol) of 3-fluorophthalic anhydride and 25 g (220 mmol) of 1,4-difluorobenzene was stirred mechanically and heated to ~50 °C to dissolve the anhydride, and then 9.5 g (71 mmol) of anhydrous $AlCl_3$ was added over a 5-min period. The reaction mixture was stirred without heating for an additional 30 min, after which another 1.0 g (7.5 mmol) of anhydrous $AlCl_3$ was added. The deep-red reaction mixture was poured slowly with stirring onto ice and 25 mL of concentrated aqueous HCl. The resulting solid was collected by suction filtration and then dissolved in 150 mL of ether. This solution was washed with water and then worked up to give 9.0 g (89%) of a pale pink solid that was recrystallized from 80 mL of benzene/hexane (1:1, v/v) to give 6.5 g (64%) of a beige solid with mp 137–140 °C. Two further recrystallizations from this same mixed solvent gave 4.5 g of nearly white crystals, presumed to be a mixture of regioisomeric keto acids (or the corresponding ketols): mp 139.5–142.5 °C; ^1H NMR (200.1 MHz) δ 7.92 (br d, 1 H, J = 7.9 Hz), 7.70–7.19 (m, 4 H), 7.04 (td, 1 H, J = 9.4, 4.4 Hz), 4.7 (br s, 1 H, OH); mass spectrum, m/e (relative intensity) 280 (M^+, 27), 167 (100).

A mixture of 0.80 g (2.9 mmol) of this keto acid product and 15 mL of polyphosphoric acid was stirred and heated at 140–145 °C for 3 h; then ~40 mL of crushed ice and water was added and the mixture was stirred overnight. The resulting solid was collected by suction filtration.

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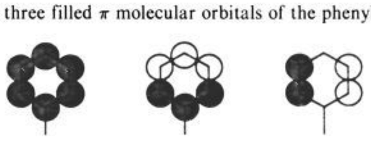
[13] As discussed in the original formuatlion of this type of theory,[6a] the 2p-based orbitals such as n_S' and n_A' would have nearly zero electron density at the two fluorine nuclei, and therefore the electrons in these orbitals would not have significant *direct* Fermi contact interactions with the fluorine nuclei. But the postulated electron spin polarization in the n_S' and n_A' orbitals would induce (by way of Hund interactions) electron spin polarization of the 1s and 2s core electrons of the fluorine atoms, and these core electrons *do* experience strong Fermi contact interactions with the fluorine nuclei. In this *indirect* way, then, antiparallel electron spin density in the n_S' and n_A' orbitals results in net Fermi contact stabilization of the antiparallel arrangement of the two fluorine nuclear spins. We have chosen to describe both the through-space F–F and F–X–F coupling phenomena in terms of the in-plane $2p_y$ fluorine lone-pair orbitals rather than the 2s fluorine lone-pair orbitals ("mostly 2s" would be a more accurate description)[9] because of our expectation[6a] that the $2p_y$ orbitals would experience greater overlap interactions than the 2s orbitals when two fluorine atoms are crowded directly together in a nonbonded way. This earlier surmise has now been confirmed by ab initio molecular orbital calculations.[14] Thus, for two HF molecules oriented in a head-to-head manner with their bond axes parallel, the calculations indicate that at an F–F separation of 2.42 Å the symmetric and antisymmetric combinations of the in-plane $2p_y$ orbitals differ in energy by 1.0 eV, whereas the symmetric and antisymmetric combinations of the 2s orbitals differ in energy by only 0.3 eV; at an F–F separation of 4.84 Å, both of these energy differences are zero. Nevertheless, we cannot rule out the possibility that overlap interactions of the 2s orbitals are a major source of through-space F–F and F–X–F coupling. It should be noted that the bonding and antibonding molecular orbitals that would be generated by overlap interactions of the 2s lone-pair orbitals on the fluorine atoms would have finite electron density at the two fluorine nuclei, and therefore the electrons in these orbitals would experience *direct* Fermi contact interactions with those nuclei.

[14] These calculations were carried out at the STO-3G level with standard geometries by Professor Michelle M. Francl of the Department of Chemistry at Bryn Mawr College.

[15] Of the three filled π molecular orbitals of the phenyl group, π_1, π_2,



and π_3, only π_1 is believed to be involved significantly in mixing with the fluorine-based n_A orbitals: π_2 does not mix appreciably because it is considerably higher in energy than n_A (by ~5.2 eV, according to calculations[14]), and π_3 has the wrong symmetry for interaction with n_A.

[16] Mallory, F. B. *J. Chem. Educ.* **1962**, *39*, 261.

[17] Heller, A. *J. Org. Chem.* **1960**, *25*, 834.

A solution of this material in 100 mL of chloroform was washed with aqueous 5% NaOH solution and then worked up to give 0.6 g (80%) of 1,4,5-trifluoroanthraquinone (**3**). Two recrystallizations of this product from benzene gave bright yellow crystals of **3**: mp 261–262 °C; ^{1}H NMR (200.1 MHz) δ 8.09 (br d, 1 H, H-4, $J_{3,4} = 7.7$ Hz), 7.78 (ddd, 1 H, H-3, $J_{2,3} = 8.3$ Hz, $J_{3,4} = 7.7$ Hz, $J_{1,3} = 4.6$ Hz), 7.50 (ddd, 1 H, H-2, $J_{1,2} = 10.6$ Hz, $J_{2,3} = 8.3$ Hz, $J_{2,4} = 1.2$ Hz), 7.55–7.43 (m, 2 H, H-6 and H-7); ^{19}F NMR (282.4 MHz) δ 1.71 (br dd, 1 F, F-1, $J_{1,2} = 10.7$ Hz, $J_{1,3} = 4.5$ Hz), −1.09 (m, 1 F, F-5,[18] $J_{5,8} = 18.1$ Hz, $J_{5,6} + J_{5,7} = 13.9$ Hz), −1.80 (m, 1 F, F-8,[18] $J_{5,8} = 18.1$ Hz, $J_{7,8} + J_{6,8} = 13.9$ Hz, $J_{1,8} = 0.8$ Hz); ^{19}F NMR (282.4 MHz, ^{1}H decoupled) δ 1.71 (d, 1 F, F-1, $J_{1,8} = 0.8$ Hz), −1.09 (d, 1 F, F-5,[18] $J_{5,8} = 18.1$ Hz), −1.80 (dd, 1 F, F-8,[18] $J_{5,8} = 18.1$ Hz, $J_{1,8} = 0.8$ Hz); mass spectrum *m/e* (relative intensity) 262 (M^+, 100); exact *m/e* calcd for $C_{14}H_5F_3O_2$ 262.0241, obsd 262.0230. Anal. ($C_{14}H_5F_3O_2$) C, H.

1,5,8-Trifluoroanthracene (2). By use of previously described methodology,[19] a mixture of 0.16 g (0.6 mmol) of 1,5,8-trifluoro-9,10-anthraquinone (**3**), 1.0 g (15 mmol) of zinc dust, 10 mg of $CuSO_4 \cdot H_2O$, and 10 mL of aqueous 20% NH_3 was stirred magnetically and heated with an oil bath at 70–75 °C for 8 h. The reaction mixture was diluted with water, and the resulting solid was collected by suction filtration. This crude product was digested with several portions of hot acetone (total, 75 mL), and the combined hot solution was filtered by gravity and rotary evaporated. The residual solid was chromatographed on alumina with hexane/benzene (4:1, v/v) as the eluent to give 0.13 g (93%) of 1,5,8-trifluoroanthracene (**2**). Recrystallization of this material from isopropanol gave needles of **2**: mp 165.2–166.6 °C; ^{1}H NMR (200.1 MHz) δ 8.93 (br s, 1 H, H-9), 8.69 (br s, 1 H, H-10), 7.86 (br d, 1 H, H-4, $J_{3,4} = 8.4$ Hz), 7.48 (ddd, 1 H, H-3, $J_{3,4} = 8.4$ Hz, $J_{2,3} = 7.6$ Hz, $J_{1,3} = 5.3$ Hz), 7.21 (br dd, 1 H, H-2, $J_{1,2} = 10.4$ Hz, $J_{2,3} = 7.6$ Hz), 7.09–7.02 (m, 2 H, H-6 and H-7); ^{19}F NMR (282.4 MHz) δ −8.22 (br ddd, 1 F, F-1, $J_{1,2} = 10.6$ Hz, $J_{1,3} = 5.4$ Hz, $J_{1,10} = 1.0$ Hz), −12.80 and −13.30 (AB q of br dd, 2 F, F-5 and F-8, $J_{5,8} = 22.8$ Hz, $J_{5,6} + J_{5,7} = J_{6,8} + J_{7,8} = 14.2$ Hz); ^{19}F NMR (282.4 MHz, ^{1}H decoupled) δ −8.22 (t, 1 F, F-1, $J_{1,5} = J_{1,8} = 1.1$ Hz), −12.80 and −13.30 (AB q of d, 2 F, F-5 and F-8, $J_{5,8} = 22.8$ Hz, $J_{1,5} = 1.1$ Hz, $J_{1,8} = 1.1$ Hz); mass spectrum, *m/e* 232 (M^+); UV (95% EtOH) λ_{max} nm 384, 364, 346, 330, 315 (sh), 252, 243. Anal. ($C_{14}H_7F_3$) C, H.

1,5,8-Trifluoro-9,10-diphenylanthracene (1). An ether solution of 1.5 g (6 mmol) of 1,5,8-trifluoro-9,10-anthraquinone (**3**) was added dropwise under nitrogen to a mechanically stirred ether solution containing a large excess of phenylmagnesium bromide. The reaction mixture was heated under reflux for 3 h and then was cooled and poured into a cold saturated aqueous solution of NH_4Cl. Workup gave an oily solid that was purified by chromatography on alumina using as the eluent hexane containing gradually increasing amounts of ether. Some late fractions of the eluate yielded 0.5 g (20%) of a mixture of the cis (53%) and trans (47%) isomers[20] of 1,5,8-trifluoro-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene: mp 257–260 °C; ^{1}H NMR (300.1 MHz) δ 7.59–7.17 (m, 24 H), 6.99 (m, 2 H, cis H-6 and H-7), 6.93 (m, 2 H, trans H-6 and H-7), 6.88 (ddd, 1 H, cis H-2, $J_{1,2} = 11.8$ Hz, $J_{2,3} = 8.1$ Hz, $J_{2,4} = 1.2$ Hz), 6.82 (ddd, 1 H, trans H-2, $J_{1,2} = 11.6$ Hz, $J_{2,3} = 7.6$ Hz, $J_{2,4} = 1.6$ Hz), 3.81 (dd, 1 H, trans 9-OH, $J_{1,9} = 5.5$ Hz, $J_{8,9} = 4.2$ Hz), 3.71 (d, 1 H, trans 10-OH, $J_{5,10} = 8.8$ Hz), 3.65 (dd, 1 H, cis 9-OH, $J_{1,9} = 6.1$ Hz, $J_{8,9} = 2.5$ Hz), 3.54 (d, 1 H, cis 10-OH, $J_{5,10} = 7.2$ Hz); ^{19}F NMR (282.4 MHz) δ 2.80 (dddd, 1 F, cis F-1, $J_{1,2} = 11.8$ Hz, $J_{1,9} = 6.1$ Hz, $J_{1,3} = 5.5$ Hz, $J_{1,8} = 1.0$ Hz), 2.61 (dddd, 1 F, trans F-1, $J_{1,2} = 11.6$ Hz, $J_{1,9} = 5.5$ Hz, $J_{1,3} = 5.5$ Hz, $J_{1,8} = 1.0$ Hz), 0.93 (m, 1 F, cis F-8, $J_{5,8} = 17.1$ Hz, $J_{1,8} = 1.0$ Hz), −0.39 (m, 1 F, trans F-8, $J_{5,8} = 17.3$ Hz, $J_{1,8} = 1.0$ Hz), −1.53 (dddd, 1 F, cis F-5, $J_{5,8} = 17.1$ Hz, $J_{5,6} + J_{5,7} = 15.4$ Hz, $J_{5,10} = 7.2$ Hz), −3.41 (dddd, 1 F, trans F-5, $J_{5,8} = 17.3$ Hz, $J_{5,6} + J_{5,7} = 15.3$ Hz, $J_{5,10} = 8.8$ Hz); GC retention times (capillary, silicone, 275 °C), trans 4.8 min, cis 5.8 min; GC/MS mass spectrum *m/e* (relative intensity), trans 418 (M^+, 12), 400 ($M^+ - H_2O$, 2), 341 ($M^+ - Ph$, 100); GC/MS mass spectrum, *m/e* (relative intensity), cis 418 (M^+, 6), 384 ($M^+ - H_2O_2$, 3), 341 ($M^+ - Ph$, 100).

A solution of 80 mg (0.19 mmol) of this 53:47 mixture of cis and trans diols in 15 mL of 97% formic acid was heated under reflux for 18 h. The solvent was evaporated, and the residual solid was purified by chromatography on alumina with benzene/hexane as the eluent followed by recrystallization from 95% ethanol to give 25 mg (34%) of 1,5,8-trifluoro-9,10-diphenylanthracene (**1**): mp 231–232 °C; ^{1}H NMR (300.1 MHz) δ 7.58–7.38 (m, 10 H, phenyl), 7.36 (dd, 1 H, H-4, $J_{3,4} = 8.8$ Hz, $J_{2,4} = 1.2$ Hz), 7.24 (ddd, 1 H, H-3, $J_{3,4} = 8.8$ Hz, $J_{2,3} = 7.3$ Hz, $J_{1,3} = 4.7$ Hz), 7.00 (ddd, 1 H, H-2, $J_{1,2} = 13.6$ Hz, $J_{2,3} = 7.3$ Hz, $J_{2,4} = 1.2$ Hz), 6.94–6.84 (m, 2 H, H-6 and H-7); ^{19}F NMR (282.4 MHz) δ 10.08 (br ddd, 1 F, F-1, $J_{1,2} = 13.6$ Hz, $J_{1,8} = 6.4$ Hz, $J_{1,3} = 4.8$ Hz), 7.01 (m, 1 F, F-8,[18] $J_{5,8} = 23.0$ Hz, $J_{1,8} = 6.4$ Hz, $J_{7,8} + J_{6,8} = 16.8$ Hz), 5.36 (m, 1 F, F-5,[18] $J_{5,8} = 23.0$ Hz, $J_{5,6} + J_{5,7} = 16.4$ Hz); ^{19}F NMR (282.4 MHz, ^{1}H decoupled) δ 10.08 (dd, 1 F, F-5,[18] $J_{5,8} = 23.0$ Hz, $J_{1,5} = 1.3$ Hz), 7.01 (dd, 1 F, F-8,[18] $J_{5,8} = 23.0$ Hz, $J_{1,8} = 6.4$ Hz), 5.36 (dd, 1 F, F-1, $J_{1,8} = 6.4$ Hz, $J_{1,5} = 1.3$ Hz); UV (95% ethanol) λ_{max} nm 403, 381.5, 362, 345 (sh), 258; mass spectrum *m/e* (relative intensity) 384 (M^+, 100); exact *m/e* calcd for $C_{26}H_{15}F_3$ 384.1126, obsd 384.1137.

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Registry No. 1, 125495-50-3; **2**, 125495-47-8; **3**, 125495-42-3; 3-fluorophthalic acid, 1583-67-1; 3-fluorophthalic anhydride, 652-39-1; 1,4-difluorobenzene, 540-36-3; 3-fluoro-2-(2,5-difluorobenzoyl)benzoic acid, 125495-43-4; 2-fluoro-6-(2,5-difluorobenzoyl)benzoic acid, 125495-44-5; 4-fluoro-3-hydroxy-3-(2,5-difluorophenyl)-3*H*-isobenzofuran-1-one, 125495-45-6; 7-fluoro-3-hydroxy-3-(2,5-difluorophenyl)-3*H*-isobenzofuran-1-one, 125495-46-7; *cis*-1,5,8-trifluoro-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, 125495-48-9; *trans*-1,5,8-trifluoro-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, 125495-49-0.

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(18) The assignments of the F-5 and F-8 signals in the ^{19}F NMR spectra of **1** and **3** were confirmed by the following observations (E. D. Luzik, Jr., and F. B. Mallory, work in progress): $J_{1,8} = 0.8$ Hz in 1,8-difluoroanthraquinone; $J_{1,5} \leq 0.4$ Hz in 1,5-difluoroanthraquinone; and $J_{1,8} = 4.6$ Hz in 1,8-difluoro-9-phenylanthracene.

(19) Golden, R.; Stock, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 3080. We are grateful to Professor Leon M. Stock of the University of Chicago for kindly bringing this procedure to our attention.

(20) The stereochemical assignments for these two diols are based on their mass spectral fragmentation patterns: the major isomer (53%) loses hydrogen peroxide but not water and is therefore assigned cis stereochemistry, whereas the minor isomer (47%) loses water but not hydrogen peroxide and is therefore assigned trans stereochemistry.