the plots of "ln (peak height)" *vs.* "*t*" were linear and showed no evidence for nonexponential decay. In general, it is likely that cross relaxation may present a more formidable problem that it has for these derivatives.

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A Theory Regarding the Role of Lone-Pair Interactions in "Through-Space" Fluorine–Fluorine Nuclear Spin–Spin Coupling

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Abstract: A theoretical description of the mechanism of "through-space" fluorine–fluorine nuclear spin–spin coupling is presented, based on the concept that two lone-pair orbitals from spatially proximate fluorines can interact by direct overlap to form one bonding and one antibonding molecular orbital delocalized over both fluorines. Positive coupling constants are explained in terms of spin-correlation effects (Hund's rule behavior) of the electrons in these two-center molecular orbitals and Fermi contact interactions of the spin-polarized fluorine core electrons. The pronounced dependence of the magnitude of this type of coupling on the distance between the two fluorines is accounted for in terms of the Pauli exclusion principle and the extent to which the bonding and antibonding orbitals differ in their electron density distributions.

The existence of a "through-space" mode of spin–spin coupling between two fluorine nuclei[1] has been convincingly demonstrated by a number of observations of large-magnitude coupling constants in molecules in which the two coupled fluorines are in close spatial proximity (*i.e.*, an F–F distance of about 2.7 Å or less) but are separated by four or more bonds.[2] The cases known thus far involve molecules of three different structural types, **1**–**3**; some examples are indicated in Figure 1.

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There are two key characteristics of this type of coupling: the magnitude of the coupling constant depends strikingly on the distance of separation of the two fluorine nuclei, as has been shown most clearly by the recent studies of Servis and Jerome;[2n,t] and the sign of the coupling constant has been found to be positive in each of the 17 reported cases in which the appropriate double or triple resonance experiments have been carried out.[2i,m,r,v]

It is the purpose of this paper to present a detailed, qualitative, theoretical formulation to explain the mechanism of "through-space" coupling between fluorine nuclei. Such an explanation has apparently not been given previously, although it has often been suggested in various ways that the overlap of a pair of 2p lone-pair orbitals at distances less than twice the van der Waals radius of fluorine or the contribution of resonance structures with a "long bond" between the fluorines is somehow involved.[1,2b,d,h,i,m,3-6]

Of the many attempts to develop quantum mechanical theories to serve as a basis for quantitatively

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(1) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(2) (a) W. S. Brey, Jr., and K. C. Ramey, *ibid.*, **39**, 844 (1963); (b) J. Jonas, L. Borowski, and H. S. Gutowsky, *ibid.*, **47**, 2441 (1967); (c) J. Jonas, *ibid.*, **47**, 4884 (1967); (d) A. Peake and L. F. Thomas, *Trans. Faraday Soc.*, **62**, 2980 (1966); (e) R. Fields, M. Green, and A. Jones, *J. Chem. Soc. B*, 270 (1967); (f) K. W. Jolley, L. H. Sutcliffe, and S. M. Walker, *Trans. Faraday Soc.*, **64**, 269 (1968); (g) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 3577 (1968); (h) K. L. Servis and K. Fang, *ibid.*, **90**, 6712 (1968); (i) R. A. Fletton, R. D. Lapper, and L. F. Thomas, *Chem. Commun.*, 1049 (1969); (j) S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, **91**, 4381 (1969); (k) F. B. Mallory, M.-C. Fedarko, and C. W. Mallory, unpublished results; (l) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970); (m) R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, **66**, 1025 (1970); (n) K. L. Servis and F. R. Jerome, *J. Amer. Chem. Soc.*, **93**, 1535 (1971); (o) M. A. Cooper, H. E. Weber, and S. L. Manatt, *ibid.*, **93**, 2369 (1971); (p) W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *J. Chem. Soc. C*, 937 (1971); (q) R. E. Banks, M. Bridge, R. Fields, and R. N. Haszeldine, *ibid.*, 1282 (1971); (r) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. ORGN-110; (s) F. J. Weigert and W. Mahler, *J. Amer. Chem. Soc.*, **94**, 5314 (1972); (t) F. R. Jerome and K. L. Servis, *ibid.*, **94**, 5896 (1972); (u) F. B. Mallory and W. M. Ricker, unpublished results; (v) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Amer. Chem. Soc.*, **95**, 975 (1973).

(3) M. T. Rogers and J. D. Graham, *ibid.*, **84**, 3666 (1962).

(4) (a) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 31–32; (b) see also W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965), for a related proposal regarding overlap interactions between fluorine lone-pair orbitals and aromatic π systems.

(5) The possibility has been raised that the magnitude of "through-space" F–F coupling is related to the energy involved in the steric repulsion of the two fluorines.[2m]

(6) (a) K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Amer. Chem. Soc.*, **94**, 4078 (1972); (b) K. Hirao, H. Nakatsuji, and H. Kato, *ibid.*, **95**, 31 (1973).

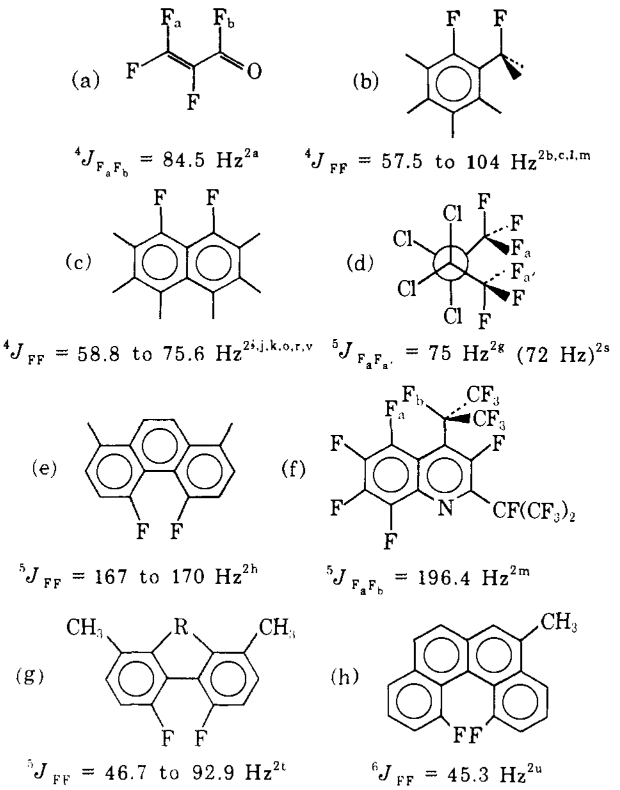


Figure 1. Some examples of "through-space" fluorine–fluorine nuclear spin–spin coupling.

meaningful calculations of coupling constants, two have specifically considered cases in which the "through-space" coupling mechanism is believed to be operative. Barfield and Karplus[7] have used perturbation theory with the average energy approximation to develop a general valence-bond formulation for nuclear spin–spin coupling in terms of Penney–Dirac bond orders; this approach, which explicitly recognizes "direct" or "through-space" interactions, could be applied in principle to F–F and other types[8] of coupling. More recently, Hirao, *et al.*,[6] have used a sum over states perturbation method[9,10] in conjunction with INDO molecular orbitals[11] to calculate F–F coupling constants in a variety of molecules and have described the type of coupling indicated in Figure 1 as "fragment coupling." Although these and other[12] mathematical formulations seem promising, the conceptual model of "through-space" coupling to be introduced in the following discussion may also prove useful.

It is generally assumed as a first approximation that the relevant filled orbitals associated with an individual fluorine atom bonded to carbon in a typical molecule are the σ_{CF} bonding orbital and the 1s, 2s, and two 2p lone-pair orbitals.[13–15] However, in molecules of structural types **1–3** the proximity of the two fluorines leads to direct overlap interaction between what are nominally classified as fluorine valence-level lone-pair orbitals; under these circumstances, a more suitable description of the molecule is obtained by replacing each pair of significantly interacting one-center orbitals by a pair of new two-center orbitals that can be represented, approximately, by the sum (bonding combination) and the difference (antibonding combination) of the overlapping lone-pair orbitals.

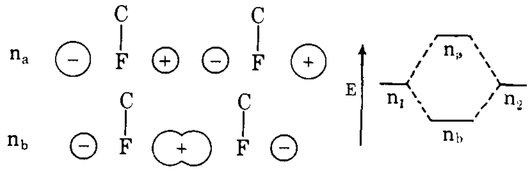
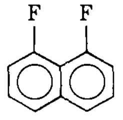


Figure 2. The shapes and relative energies of the bonding and antibonding molecular orbitals, $n_b = n_1 + n_2$ and $n_a = n_1 - n_2$, respectively, resulting from the interaction by direct σ overlap of two in-plane 2p atomic orbitals, n_1 and n_2, centered on spatially proximate fluorines.

To illustrate the way in which "through-space" F–F coupling is here postulated to depend on this type of lone-pair interaction, it is convenient to consider first the specific example of 1,8-difluoronaphthalene (**4**);



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after the theory has been fully developed with reference to this particular type **1** system, the generalization of the theory to include systems of types **2** and **3** will be presented.

It is assumed for simplicity that the two C–F bonds in **4** are parallel and the F–F distance is 2.5 Å. From a tabulation of overlap integrals[17] determined by calculations based on Slater orbitals, the following values are obtained for the fluorine lone-pair orbitals in this system: 0.009 for the σ overlap of the two in-plane $2p_y$ orbitals; 0.003 for the σ overlap of the two 2s orbitals; and a negligibly small value for the π overlap of the two out-of-plane $2p_x$ orbitals. The actual ratio of $2p_y$–$2p_y$ overlap to 2s–2s overlap is presumably even larger than 0.009:0.003, since for large internuclear separations (such as 2.5 Å for two fluorines) calculations based on Slater orbitals are known[17] to underestimate the former but not the latter overlap compared to calculations based on SCF orbitals. Consequently, it seems justifiable to simplify the discussion of **4** by neglecting the 2s–2s overlap and considering that only the two in-plane atomic $2p_y$ orbitals, n_1 and n_2, need to be replaced by

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(7) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

(8) G. R. Miller, A. W. Yankowsky, and S. O. Grim, *J. Chem. Phys.*, **51**, 3185 (1969).

(9) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(11) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(12) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *ibid.*, **49**, 2965 (1968).

(13) Because of the large energy gap between the 2s and 2p orbitals for fluorine, the extent of hybridization is expected to be small: see D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *ibid.*, **32**, 196 (1960), and also H. Konishi and K. Morokuma, *J. Amer. Chem. Soc.*, **94**, 5603 (1972).

(14) The present discussion is also compatible with the assumption that the lone-pair orbital here designated as 2s is actually a hybrid orbital with a small contribution from the $2p_z$ orbital oriented along the C–F bond axis as suggested for HF by C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964), and also by C. F. Bender and E. R. Davidson, *ibid.*, **47**, 360 (1967).

(15) The well-recognized[16] delocalization of lone-pair electrons over the molecular framework by interaction with suitable σ or π orbitals will be considered later.

(16) For example, see R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971), and C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **94**, 1466 (1972).

(17) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

$$\text{(a)}\quad F_1[n_b\uparrow n_a\uparrow]F_2[n_b\downarrow n_a\downarrow]$$

$$\text{(b)}\quad F_1[n_b\uparrow n_a\downarrow]F_2[n_b\downarrow n_a\uparrow]$$

$$\text{(c)}\quad F_1[n_b\uparrow n_b\downarrow]F_2[n_a\uparrow n_a\downarrow]$$

Figure 3. Diagrammatic representations of three possible types of instantaneous electron configuration for a system of four electrons in two different orbitals, n_b and n_a, both of which encompass two fluorine nuclei, F_1 and F_2.

$$\text{(a)}\quad F_1\downarrow[s\uparrow][n_b\uparrow n_a\uparrow]F_2\uparrow[s\downarrow][n_b\downarrow n_a\downarrow]$$

$$\text{(b)}\quad \underbrace{F_1\uparrow[s\uparrow]}_{\substack{\text{destabilizing}\\ \text{Fermi contact}\\ \text{interaction}}}[n_b\uparrow n_a\uparrow]F_2\uparrow[s\downarrow][n_b\downarrow n_a\downarrow]$$

$$\text{(c)}\quad F_1\uparrow\underbrace{[s\downarrow][n_b\uparrow n_a\uparrow]}_{\substack{\text{destabilizing}\\ \text{Hund interaction}}}F_2\uparrow[s\downarrow][n_b\downarrow n_a\downarrow]$$

Figure 4. Representations of the energetically preferred instantaneous electron spin configurations for a system of two filled two-center molecular orbitals, n_b and n_a, associated with two fluorine nuclei, F_1 and F_2. If the nuclear spins are antiparallel, the electrons can adopt a configuration that optimizes all Hund and Fermi interactions as shown in example a. If the nuclear spins are parallel, the lowest energy arrangement for Hund interactions would have one destabilizing Fermi interaction as shown in example b, and the lowest energy arrangement for Fermi interactions would have one destabilizing Hund interaction as shown in example c.

the bonding and antibonding molecular orbitals, $n_b = n_1 + n_2$ and $n_a = n_1 - n_2$, respectively. These molecular orbitals and their relative energies are illustrated schematically in Figure 2. Since both the bonding (n_b) and antibonding (n_a) orbitals are filled, there is no net F–F bonding. In fact, n_a would be destabilized relative to n_1 and n_2 more than n_b would be stabilized, and therefore the molecule as a whole should experience net destabilization as a consequence of the interaction of the two crowded fluorines.[18]

The transmittal of nuclear spin information from one fluorine to the other by way of the n_b and n_a electrons can be understood by considering two factors: the distribution of spin density within the n_b and n_a orbitals, and the influence of the n_b and n_a electrons on the spin density at each of the fluorine nuclei by core polarization effects.

Electron–electron repulsions will be minimized in the n_b and n_a orbitals if the electrons are evenly distributed with two of them in the region closer to nucleus 1 and the other two in the region closer to nucleus 2. As indicated in Figure 3, the two electrons around a particular nucleus at a given instant could have either parallel spins (Figure 3a) or antiparallel spins (Figures 3b and 3c). The first type of instantaneous configuration (Figure 3a) would be favored over the other two types on energetic grounds according to Hund's rule (this point is elaborated further with reference to the Pauli exclusion principle later in the discussion). That is, two electrons occupying separate but spatially overlapping orbitals in the vicinity of a particular nucleus are better able to avoid each other if their spins are parallel rather than antiparallel, and hence Coulombic repulsions are smaller in the parallel-spin case.

Direct Fermi contact interaction of the four electrons in the n_b and n_a orbitals with the two fluorine nuclei is not expected to be important since those orbitals would retain, as a first approximation, the nodes at the nuclei that are characteristic of the $2p_y$ orbitals from which they can be considered to be constructed. However, an n_b or n_a electron could interact indirectly with a fluorine nucleus by inducing spin polarization of the electrons in that fluorine's 1s and 2s core orbitals to give a nonzero electron spin density at the nucleus; this would result in either a favorable or an unfavorable Fermi contact interaction, depending on whether the net 1s and 2s electron spin density at the nucleus were antiparallel or parallel, respectively, to the nuclear spin. Of the types of configuration of the n_b and n_a electrons under consideration, only that shown in Figure 3a would give rise to significant Fermi contact interactions by this core polarization mechanism; in the configurations shown in Figures 3b and 3c, the two electrons with opposed spins associated with each fluorine would have counteracting core polarization effects. Since the n_b and n_a orbitals are both expected to resemble atomic 2p orbitals rather closely in the vicinity of each fluorine, it seems reasonable to use the spin polarization effects of a 2p electron in an isolated fluorine atom as a model for the spin polarization effects of an n_b or n_a electron in a molecule like **4**. Unrestricted Hartree–Fock calculations[19] on a fluorine atom in its ground state electron configuration, $1s^2 2s^2 2p^5$, show that an unpaired 2p ↑ electron interacts with the two inner shell 1s electrons such that the probability of being at the nucleus is greater for the 1s ↓ electron than for the 1s ↑ electron (a condition designated as negative spin density); these same calculations show that an unpaired 2p ↑ electron influences the 2s electrons in the opposite sense, with the 2s ↑ electron having a greater probability of being at the nucleus than the 2s ↓ electron (positive spin density). The calculated magnitude of the effect is larger for the 2s electrons than for the 1s electrons, so the net effect of a 2p ↑ electron is to induce positive s orbital spin density, s ↑, at the nucleus.[19,20] On this basis, then, the instantaneous electron spin configuration shown in Figure 3a would give rise to net s ↑ spin density at the nucleus of the fluorine associated with the $n_b\uparrow$ and $n_a\uparrow$ electrons and net s ↓ spin density at the nucleus of the fluorine associated with the $n_b\downarrow$ and $n_a\downarrow$ electrons.

It follows from the preceding analysis that only a system with antiparallel spins of the two fluorine nuclei, F_1 and F_2, will be stabilized by Fermi contact interactions. Thus, with antiparallel nuclear spins it is possible for the n_b, n_a, and core s electrons to adopt

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(18) Thus, the interaction being considered here differs from the stabilizing "p–p interaction" based on dispersion forces discussed in ref 4.

(19) D. A. Goodings, *Phys. Rev.*, 123, 1706 (1961).

(20) In order to account for the negative signs observed experimentally for various one-bond coupling constants such as those between carbon-13 and fluorine, it was proposed by C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **51**, 2790 (1969), that the net effect of a $\sigma_{CF}\uparrow$ electron in a carbon–fluorine σ bond, in contrast to a $2p\uparrow$ electron on an isolated fluorine atom, is to induce *negative* s orbital spin density, $s\downarrow$, at the fluorine nucleus. These authors justified this proposal by reasoning that a σ_{CF} orbital is more expanded away from the fluorine (toward the carbon) than a 2p orbital, which should make the fluorine 2s orbital behave more like an inner shell[21] 1s orbital in its response to the spin polarizing influence of a σ_{CF} electron.

(21) D. A. Goodings and V. Heine, *Phys. Rev. Lett.*, **5**, 270 (1960).

the preferred spin distribution described above, in which all Hund interactions between electrons are optimal, and also for both nuclei to experience the energetically more favorable Fermi contact interaction; this is indicated by the example shown diagrammatically in Figure 4a. In contrast, a system with parallel nuclear spins would have at least one destabilizing interaction: if the n_b, n_a, and core s electrons were to adopt a spin distribution that allows the preferred Hund interactions for all of these electrons, then one of the nuclei would experience a destabilizing Fermi interaction as exemplified in Figure 4b; and if the system adopted the preferred Fermi interactions at both nuclei, then there would be a destabilizing Hund interaction around one of the fluorines as exemplified in Figure 4c. By virtue of this prediction of a more favorable set of spin interactions for antiparallel as compared to parallel nuclear spins, the present theoretical formulation successfully accounts for the experimental observations that "through-space" F–F coupling constants are positive in sign.

It is further theorized that the magnitude of the "through-space" contribution to the F–F coupling constant in a molecule like **4** depends on the probability that the n_b and n_a electrons can be distributed as shown in Figures 3a and 4, with both spin-up electrons associated with one fluorine and both spin-down electrons associated with the other fluorine. The arguments that follow show how this probability can be related to the extent of interaction between the overlapping n_1 and n_2 orbitals.

In the limiting case in which one could consider the n_1 and n_2 orbitals to have no direct overlap interaction (*e.g.*, with a significantly longer F–F distance than the value of 2.5 Å considered thus far), the distribution of electron density in n_b would be identical with that in n_a in the neighborhood of each individual fluorine nucleus, where both molecular orbitals would in fact have the spatial characteristics of unmodified 2p atomic orbitals. In this limiting situation, it would be a violation of the Pauli exclusion principle to have two electrons of the same spin around a particular nucleus; thus, even though these electrons would occupy formally different orbitals, n_b and n_a, the wave functions governing the two electrons would have locally identical space parts and would therefore be required by the Pauli principle to have locally different spin parts. Another way of arriving at this conclusion is to consider that in the absence of any interaction between n_1 and n_2, the description in terms of n_b and n_a is only a symmetry-adapting device that would have no influence on the physical properties of the system; then by a more familiar application of the Pauli principle it is seen that the existence of two electrons with parallel spin in an orbital such as n_1 or n_2 would be disallowed. Therefore, for difluoro molecules lacking any appreciable overlap between the n_1 and n_2 orbitals, configurations of the type $F_1[n_b\uparrow n_a\uparrow]$ would have zero probability and "through-space" F–F coupling should not be operative.

At the other extreme, one can imagine a molecule having two severely crowded fluorines with extensive overlap between the n_1 and n_2 orbitals such that the distribution of electron density in the n_b orbital could be quite different from that in the n_a orbital. (One such difference would be that the electron density in the region between the two fluorines would be greater in n_b than in n_a as indicated in Figure 2.) Conceivably, the spatial difference between the n_b and n_a orbitals could be sufficiently pronounced that the $F_1[n_b\uparrow n_a\uparrow]$ arrangement would not be forbidden by the Pauli exclusion principle (no more so, for example, than the C $1s^22s^22p_x\uparrow 2p_y\uparrow$ configuration of an isolated carbon atom). In fact, from a simple application of Hund's rule, as given earlier in the discussion regarding Figure 3, it would follow that for a molecule of this type the probability of a configuration involving $F_1[n_b\uparrow n_a\uparrow]$ would be greater than that of a configuration involving $F_1[n_b\downarrow n_a\uparrow]$.

For molecules falling between these two extremes, it seems reasonable to propose that the extent to which the probability of the $F_1[n_b\uparrow n_a\uparrow]$ arrangement would exceed zero would be a smooth and gradually increasing function of the extent to which the n_b and n_a orbitals would differ in their electron density distributions. That is, one might expect that the forbidden character of the $F_1[n_b\uparrow n_a\uparrow]$ arrangement that is required by the Pauli principle for rigorously noninteracting n_1 and n_2 orbitals would not completely disappear in a system having only an infinitesimal amount of overlap interaction of these two orbitals. Unfortunately, it is not possible here to suggest a way of putting this proposed relationship between Pauli forbiddenness and orbital overlap on a sound quantitative basis. However, as a speculative *ad hoc* hypothesis, it is postulated that in the particular case of the molecule **4**, and in general in all molecules of types **1**, **2**, and **3** in which "through-space" F–F coupling is operative, the overlap of the n_1 and n_2 lone-pair orbitals is sufficiently small in magnitude that electron configurations of the type shown in Figures 3a and 4 are only partially allowed by the Pauli principle.

In recapitulation, it is hypothesized that the degree to which the electron configurations shown in Figures 3a and 4 are allowed by the Pauli principle, which would govern the magnitude of the F–F coupling constants in these systems, depends on the degree to which the n_b and n_a orbitals differ in their electron density distributions, which would be governed by the magnitude of the overlap interaction[22] between the n_1 and n_2 orbitals. In this way, the theoretical coupling mechanism presented here can account for the experimentally observed[1,2] dependence of the magnitude of "through-space" F–F coupling on the distance between the two fluorines. Furthermore, by focusing on orbital overlap as the important feature, this theory predicts that "through-space" F–F coupling constants will be influenced not only by the distance between the two fluorine nuclei but also by the angular orientation of the two C–F bonds.

To generalize this theory to include systems of types **2** and **3**, it is necessary to take into account the interactions of all three kinds of fluorine lone-pair orbitals. For example, in the particular cases of 4,5-difluorophenanthrene (**5**) and 1,12-difluorobenzo[*c*]phenanthrene (**6**), the mixed σ–π overlap of the two "out-of-plane" $2p_x$ orbitals, the mixed σ–π overlap of the two "in-plane" $2p_y$ orbitals, and the σ overlap of the two 2s

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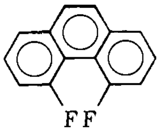
[22] One measure of this magnitude would be the energy difference between the n_b and n_a orbitals, a quantity obtainable in principle from molecular orbital calculations or photoelectron spectroscopy.



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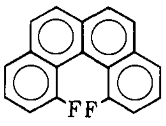

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orbitals are all expected to be significant in magnitude. (Molecules **5** and **6** are precluded from overall planarity by steric factors; the terms "out-of-plane" and "in-plane" as used here refer to the approximately planar local environments around each individual fluorine, including the fluorine, the carbon to which it is directly bonded, and the two adjacent ring carbons.) The molecular orbitals of interest for these systems are approximated in the usual way by the sums and differences of the overlapping atomic orbitals as indicated in the following list.

$$n_b(2p_x) = n_1(2p_x) + n_2(2p_x)$$

$$n_a(2p_x) = n_1(2p_x) - n_2(2p_x)$$

$$n_b(2p_y) = n_1(2p_y) + n_2(2p_y)$$

$$n_a(2p_y) = n_1(2p_y) - n_2(2p_y)$$

$$n_b(2s) = n_1(2s) + n_2(2s)$$

$$n_a(2s) = n_1(2s) - n_2(2s)$$

On the basis of the analysis of the 2p-derived molecular orbitals of **4** given earlier in this discussion, one expects that the set of $n_b(2p_x)$ and $n_a(2p_x)$ orbitals on the one hand, and also the set of $n_b(2p_y)$ and $n_a(2p_y)$ orbitals on the other hand, would each provide stabilization for a system of antiparallel nuclear spins as compared to parallel nuclear spins if the two sets of orbital electrons were to act independently (see Figure 4). Regarding their joint behavior, the question is whether they would reinforce or counteract each other's spin-polarizing influence on the fluorine core s electrons; the answer to this question is given by Hund's rule, by which one predicts that whenever the $n_b(2p_x)\uparrow$ and $n_a(2p_x)\uparrow$ electrons are preferentially located in the vicinity of one of the two fluorines, then it would be energetically more favorable for the $n_b(2p_y)\uparrow$ and $n_a(2p_y)\uparrow$ electrons, rather than the $n_b(2p_y)\downarrow$ and $n_a(2p_y)\downarrow$ electrons, to be located around that same fluorine. Thus, the two sets of 2p-derived molecular orbitals act in concert to favor the antiparallel configuration of nuclear spins as indicated in the example shown in Figure 5a.

Turning now to consider the $n_b(2s)$ and $n_a(2s)$ orbitals, one can argue once again on the basis of Hund's rule that the energetically favored electron configurations have both spin-up electrons around one fluorine and both spin-down electrons around the other fluorine. Unlike the previous cases of 2p-derived molecular orbitals, the 2s-derived $n_b(2s)$ and $n_a(2s)$ orbitals would each have significant electron density at the two fluorine nuclei, and hence the electrons in these molecular orbitals would be involved in direct Fermi contact interactions with the nuclei. Thus, the configuration with antiparallel nuclear spins shown in Figure 5b would represent the optimum arrangement for the system considering only the influence of the $n_b(2s)$ and $n_a(2s)$ electrons. The contribution of these electrons toward the stabilization of antiparallel rather than parallel nuclear spins would enhance the contribution made by the electrons in the four 2p-derived orbitals according to Hund's rule; thus, it would be energetically preferred for the $n_b(2s)\uparrow$ and $n_a(2s)\uparrow$ electrons to be associated with the same fluorine as the $n_b(2p_x)\uparrow$, $n_a(2p_x)\uparrow$, $n_b(2p_y)\uparrow$, and $n_a(2p_y)\uparrow$ electrons. As can be seen in Figures 5a and 5b, this means that all six of these electrons would favor the F ↓ spin orientation of that fluorine nucleus.

$$\text{(a)}\quad F_1\downarrow[s\uparrow][n_b(2p_x)\uparrow n_a(2p_x)\uparrow][n_b(2p_y)\uparrow n_a(2p_y)\uparrow]$$

$$F_2\uparrow[s\downarrow][n_b(2p_x)\downarrow n_a(2p_x)\downarrow][n_b(2p_y)\downarrow n_a(2p_y)\downarrow]$$

$$\text{(b)}\quad F_1\downarrow[n_b(2s)\uparrow n_a(2s)\uparrow]F_2\uparrow[n_b(2s)\downarrow n_a(2s)\downarrow]$$

Figure 5. Energetically preferred nuclear electron spin configurations with optimum Fermi and Hund interactions for a system of two fluorine nuclei, F_1 and F_2, and the electrons in the two-center molecular orbitals generated by overlap interactions of the $2p_x$ and $2p_y$ fluorine lone-pair orbitals (a) and also the 2s fluorine lone-pair orbitals (b). See text for explanation.

It can be concluded that all three kinds of lone-pair interactions act in a cooperative fashion in their selective stabilization of systems with antiparallel spins of the two fluorine nuclei. Therefore, the arguments and concepts that were used previously in the presentation of the F–F coupling theory for the special case of **4**, a system in which it was assumed that only one of these three interactions was important, are also applicable to the general case.

"Through-bond" interactions of two lone-pair orbitals on different atoms, which involve the overlap of these orbitals with adjacent σ or π molecular orbitals, are well established on the basis of recent work.[16,23] In the molecular orbital description of "through-space" F–F coupling given above, it was proposed that the key requisite for coupling is the existence of spatially different n_b and n_a orbitals. Clearly, this type of spatial difference could be induced by indirect "through-bond" interactions of the n_1 and n_2 lone-pair orbitals[24] as well as by direct "through-space" interactions of the type already considered. Although it seems very likely that "through-space" lone-pair interactions are dominant in the F–F coupling in systems of types **2** and **3**, it may be that both "through-space" and "through-bond" lone-pair interactions are important in the F–F coupling in systems of type **1**. "Through-bond" interactions between fluorine lone pairs may contribute significantly to the observed[25] five-bond F–F coupling constant of 19 Hz in 1,4-difluorobicyclo[2.2.2]octane; the structure of this molecule is particularly well suited

[23] (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969); (c) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **92**, 3506 (1970); (d) E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, **53**, 331 (1970); (e) E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970); (f) R. Gleiter, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **9**, 901 (1970); (g) J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970); (h) A. D. Jordan, I. G. Ross, R. Hoffmann, J. R. Swenson, and R. Gleiter, *Chem. Phys. Lett.*, **10**, 572 (1971); (i) D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **10**, 401 (1971); (j) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5599 (1972).

[24] The "through-bond" coupling mechanism being considered here, which involves spin polarization in the bonding and antibonding pair of molecular orbitals whose electron density is largely concentrated on the two fluorines, differs from the traditional "through-bond" coupling mechanism involving spin polarization in the bonding orbitals of the molecular framework.

[25] (a) J. C. Kauer, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **15**, B14 (1970); (b) see ref 2s for an alternative interpretation.

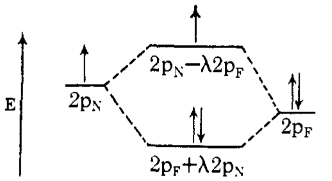
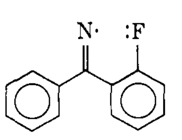


Figure 6. Orbital energies and occupancies for radical **7**, both in classical terms involving the one-center orbitals $2p_N$ and $2p_F$, and also in molecular orbital terms involving the two-center orbitals $2p_F + \lambda 2p_N$ and $2p_N - \lambda 2p_F$.

for such interactions,[16,23] and the F–F distance is too large for appreciable "through-space" interactions.

Finally, the same general approach that was used in the preceding discussion to treat "through-space" coupling between two fluorine nuclei as a two-orbital, four-electron problem can also be used to treat "through-space" coupling between an odd electron and a fluorine nucleus (or any other magnetic nucleus of an atom with an appropriately oriented lone-pair orbital) as a two-orbital, three-electron problem. Examples of this latter type of coupling are provided by radicals **7**[26] and **8**,[27] which are structurally related to the systems of types **1** and **2**, respectively, that were considered earlier. Classically, radical **7** is formulated with an odd electron in an in-plane $2p_N$ orbital on nitrogen and a lone pair of electrons in an in-plane $2p_F$ orbital on fluorine. An approximate molecular orbital description of **7** is obtained by replacing these two spatially overlapping atomic orbitals by a pair of two-center molecular orbitals, $2p_F + \lambda 2p_N$ and $2p_N - \lambda 2p_F$ with $0 < \lambda < 1$, as indicated in Figure 6. The presence of an odd electron in the $2p_N - \lambda 2p_F$ orbital in **7** would place significant electron spin density around the fluorine, which would account for the large hyperfine splitting by the fluorine nucleus that has been reported for this radical.[26] The large hyperfine interactions found[27] for radical **8** can be accounted for by an entirely analogous molecular orbital treatment, using as the basis set the in-plane 2p orbital on oxygen and the in-plane 2p orbital on fluorine. Basically this same explanation, expressed in different terms, has been offered previously for hyperfine interactions of this type.[26–28]



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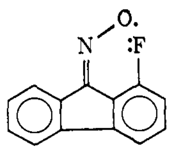

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(26) R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *Chem. Commun.*, 721 (1972).

(27) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 722 (1966).

(28) (a) P. J. Scheidler and J. R. Bolton, *J. Amer. Chem. Soc.*, **88**, 371 (1966); (b) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 981 (1967); (c) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); (d) E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **89**, 4902 (1967); (e) F. A. Neugebauer, *Tetrahedron Lett.*, 2345 (1970); (f) M. Iwasaki, *Mol. Phys.*, 20, 503 (1971).

On the Mechanism of Phenolic Oxidative Coupling Reactions. Ferricyanide Oxidation of 2,3′,4-Trihydroxybenzophenone, an Example of a Radical Aromatic Substitution Mechanism[1]

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Abstract: A thorough uv spectrophotometric kinetic study of the oxidation of 2,3′,4-trihydroxybenzophenone (**1**) by alkaline ferricyanide has been performed under pseudo-first-order conditions. Experimental observations and conclusions concerning the kinetics and mechanism of this system include the following: (1) the reaction is first order in the benzophenone **1**; (2) a nearly quantitative yield of 2,6-dihydroxyxanthone is always formed under a variety of conditions; the yield of the isomeric 3,5-dihydroxyxanthone is always less than 5%; (3) values for the three pK_a's of **1** were determined, using a spectrophotometric technique, to be 12.20, 9.24, and 7.02, respectively; (4) a curious, unexplained "tailing in" phenomenon is observed on some first-order kinetic plots; added CN^- and some other anions eliminate this unusual behavior, and all important experiments were run under conditions which minimized this initial deviation from linearity; (5) a large increase in reaction rate with increasing ionic strength is noted; (6) specific cations catalyze the reaction, increasing in effectiveness in the order $Na^+ < K^+ < Cs^+$; (7) the oxidation is strictly first order in ferricyanide under all conditions; (8) inhibition by ferrocyanide is always observed; (9) the rate increases markedly as the pH is increased. A radical aromatic substitution mechanism is proposed to be the only process consistent with all the experimental observations. These experiments constitute the first documented example of such a mechanism being involved in a phenolic oxidation coupling reaction.

Phenolic oxidative coupling is an important step in the biosynthesis of many naturally occurring compounds.[2] In the presence of a variety of chemical

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(1) Taken in part from the Ph.D. Thesis of P. D. McD., The Pennsylvania State University, 1970; Preliminary report: Fifth MARM, American Chemical Society, Newark, Del., April 2, 1970, Organic Abstract No. 29. This work was supported in part by a fellowship to P. D. McD., 1969–1970, from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and in part by a research grant from the National Science Foundation.

(2) W. I. Taylor and A. R. Battersby, "Oxidative Coupling of Phenols," Marcel Dekker, New York, N. Y., 1967.