

m/e 124. *Anal.* Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.10; H, 9.93.

Electrolysis of 8 in AcOH Containing Et_4NOH . A mixture of 7.0 g (0.05 mol) of **8**, 1.5 g of 10% aqueous Et_4NOH , and 30.0 g (0.50 mol) of acetic acid was electrolyzed. The isolated yields of **8a** and **8b** were 0.9 and 31%, respectively.

Electrolysis of 8 in AcOH- H_2O . Two kinds of solvents (commercial glacial acetic acid and 55% aqueous acetic acid) were used. Products, **8a** and **8b**, were obtained in each case. The yields of **8a** and **8b** were determined by vpc after 2 faraday/mol of electricity was passed (see Table II).

Electrolysis of 8 in CH_3CN . The reactions were carried out in two kinds of solvents (100% acetonitrile and 55% aqueous acetonitrile). The products, **8a** and **8b**, were identified by comparison of vpc retention times and ir spectra with those of authentic samples. The yields of **8a** and **8b** were determined by vpc (Table II).

Electrolysis of 8 in $CH_3CH_2CO_2H$. Two kinds of solvents (100% propionic acid and 65% aqueous propionic acid) were used. Products were **8a**, **8b**, and **8b'**. Compounds **8a** and **8b** were identified by comparison of vpc retention times and ir spectra with those of authentic samples. **8b'**: ir 1720 and 1180 cm^{-1} (ester); nmr (CCl_4) τ 4.95 (m, 1, $CHOCO$), 7.30–8.50 (m, 10, CH_2), and 8.80 (t, 3, CH_3). *Anal.* Calcd for $C_9H_{14}O_2$: C, 63.51; H, 8.29. Found: C, 63.73; H, 8.48.

Polarographic Oxidation Potential. All polarographic data were obtained at room temperature on an Yanaco P-8DP (Yanagimoto Co. Ltd). Oxidations were carried out in dry acetonitrile at a rotating platinum electrode with 0.1 M $LiClO_4$ as a supporting electrolyte using an aqueous saturated calomel reference electrode. The concentration of substrates was 2×10^{-4} M and an H-type electrolysis cell was used. All enol esters showed one oxidation wave. The results are shown in Table III.

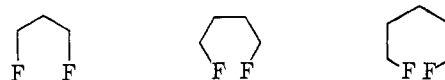
Substituent Effects on Through-Space ^{19}F - ^{19}F Coupling in the 1,8-Difluoronaphthalene System

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Contribution from the Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010. Received November 5, 1973

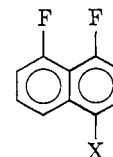
Abstract: F-F coupling constants for a series of 4-substituted 1,8-difluoronaphthalenes were determined from measurements of the ^{19}F nmr spectra of these compounds. Arguments are presented that the observed variation of J_{FF} with substituent reflects primarily a steric effect of the C-4 substituent on the F-F distance and hence on the through-space F-F coupling in this system.

Through-space interactions^{2,3} are believed to be chiefly responsible for the especially large fluorine-fluorine nuclear spin-spin coupling constants that have been observed for intramolecularly crowded fluorines in many different systems of the three structural types shown below.⁴ A few selected examples of through-space F-F coupling are indicated in Figure 1.



An earlier study^{4b} of a series of substituted 4,5-difluorophenanthrenes (see Figure 1) revealed that J_{FF} was quite insensitive to the nature of the substituent although the fluorine chemical shifts varied considerably. As a generalization of this result, it was suggested that the lack of response of the value of J_{FF} to changes in substituent, when ^{19}F chemical shifts are significantly influenced by those changes, might be a distinguishing criterion for through-space F-F coupling.^{4b} We report herein our studies of F-F coupling in a series of 4-substituted 1,8-difluoronaphthalenes, the results of which have led us to propose that the above-mentioned criterion should be qualified.

Syntheses. The 4-substituted 1,8-difluoronaphthalenes **1–8** were synthesized by the reactions outlined in



- | | |
|------------------------|----------------------------|
| 1, X = H | 5, X = NO ₂ |
| 2, X = Br | 6, X = NH ₂ |
| 3, X = CN | 7, X = NHCOCH ₃ |
| 4, X = CH ₃ | 8, X = Cl |

Scheme I. The best route that we found for the synthesis of **1** involves a Schiemann reaction starting with the readily available 1,8-diaminonaphthalene. Initially

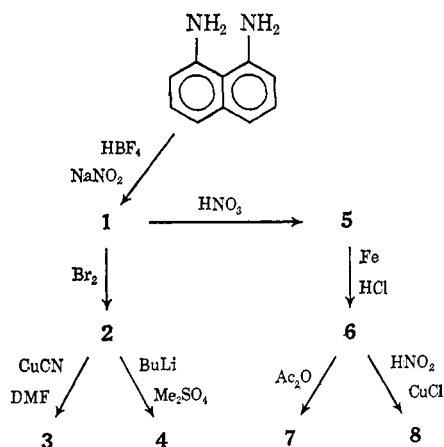
(1) Taken in part from the Senior Honors Paper of M.-C. F., Bryn Mawr College, 1969.

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

(3) For recent theoretical views of these interactions, see (a) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969); (b) K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *ibid.*, **94**, 4078 (1972); (c) K. Hirao, H. Nakatsuji, and H. Kato, *ibid.*, **95**, 31 (1973); (d) F. B. Mallory, *ibid.*, **95**, 7747 (1973).

(4) (a) W. S. Brey, Jr., and K. C. Ramey, *J. Chem. Phys.*, **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) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970); (l) R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, **66**, 1025 (1970); (m) K. L. Servis and F. R. Jerome, *J. Amer. Chem. Soc.*, **93**, 1535 (1971); (n) M. A. Cooper, H. E. Weber, and S. L. Manatt, *ibid.*, **93**, 2369 (1971); (o) W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *J. Chem. Soc. C*, 937 (1971); (p) R. E. Banks, M. Bridge, R. Fields, and R. N. Haszeldine, *ibid.*, 1282 (1971); (q) 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; (r) F. J. Weigert and W. Mahler, *J. Amer. Chem. Soc.*, **94**, 5314 (1972); (s) F. R. Jerome and K. L. Servis, *ibid.*, **94**, 5896 (1972); (t) F. B. Mallory and W. M. Ricker, unpublished results; (u) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Amer. Chem. Soc.*, **95**, 975 (1973).

Scheme I

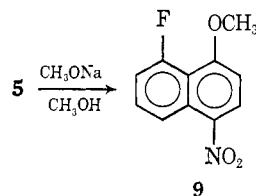


this reaction gave very low and erratic yields, but after exploring many different modifications of reaction conditions we eventually developed a procedure by which a 24% yield of **1** was achieved. The extraordinarily high volatility of **1** is also a problem in its handling. All of the other steps in Scheme I are synthetically straightforward.

Structure Assignments. The conclusion that the substituent, X, is located at the C-4 position in each of the 1,8-difluoronaphthalenes **2–8** is based on arguments in three different categories: methods of synthesis, proton nmr spectra, and fluorine nmr spectra.

Firstly, both bromination and nitration of 1-fluoronaphthalene have been reported to give the corresponding 4-substituted compounds, 4-bromo-1-fluoronaphthalene and 4-nitro-1-fluoronaphthalene, as the only isolated products and in high percentage yields.⁵ This represents strong precedent for our assignment of the 4-substituted structures **2** and **5** to the products that we obtained in high yields from the bromination and nitration, respectively, of 1,8-difluoronaphthalene.

Secondly, the proton nmr spectra of **2**, **3**, **4**, **5**, and **8** provide evidence that these compounds possess a single peri proton, since each spectrum exhibits a one-proton set of signals with the appropriate splitting at distinctly lower field than the remaining signals.⁶ This conclusion is particularly clear for the cyano compound **3** and the nitro compound **5**, both of which have proton spectra that can be analyzed completely using first-order approximations; the parameters obtained in this way are listed in Table I. Further support for the structure of **5** was obtained from the first-order analysis (see Table I) of the proton spectrum of **9**, the compound



prepared by treating **5** with sodium methoxide in methanol under conditions known to convert 1-fluoro-4-nitronaphthalene to 1-methoxy-4-nitronaphthalene.⁵

The third line of evidence in support of our structure

(5) G. Schiemann, W. Gueffroy, and W. Winkelmueller, *Justus Liebigs Ann. Chem.*, **487**, 270 (1931).

(6) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 204–207.

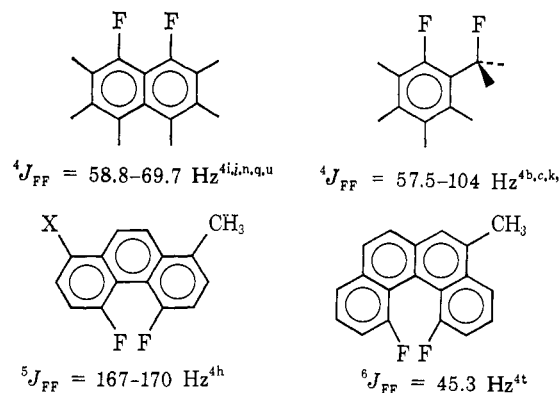
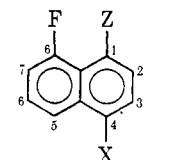


Figure 1. Some examples of through-space coupling between fluorine nuclei.

Table I. Some Proton Chemical Shifts and Coupling Constants



3, X = CN; Z = F

5, X = NO₂; Z = F

9, X = NO₂; Z = OCH₃

| Parameter ^{a,b} | 3 ^c | 5 ^d | 9 ^e |
|--------------------------|-----------------------|-----------------------|-----------------------|
| ν_2 | 432.8 | 431.7 | 405.0 |
| ν_7 | 437.9 | 436.7 | 427.5 |
| ν_6 | 460.1 | 460.1 | 452.1 |
| ν_8 | 474.6 | 493.4 | 494.3 |
| ν_5 | 482.3 | 500.7 | 503.7 |
| J_{21} | 10.9 | 10.4 | |
| J_{23} | 8.2 | 8.6 | 8.9 |
| J_{31} | 4.6 | 4.4 | |
| J_{51} | 2.1 | 2.2 | |
| J_{56} | 8.2 | 8.6 | 8.6 |
| J_{57} | 1.4 | 1.3 | 1.2 |
| J_{67} | 7.7 | 7.8 | 7.7 |
| J_{68} | 4.9 | 5.3 | 5.2 |
| J_{75} | 11.2 | 11.2 | 12.6 |

^a Proton spectra were measured at 60 MHz. Chemical shifts are given in Hz downfield from tetramethylsilane as an internal standard, and coupling constants are given in Hz. Each of the reported H–F coupling constants was confirmed by the corresponding splitting in the ¹⁹F spectrum. ^b Only the first-order magnitudes of the coupling constants are reported. Except for J_{51} , whose sign is uncertain, these coupling constants are presumed to be positive by analogy with related aromatic systems: R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Chem. Soc. B*, 835 (1967); R. J. Abraham and M. A. Cooper, *ibid.*, 1094 (1968); J. E. Loemker, J. M. Read, Jr., and J. H. Goldstein, *J. Phys. Chem.*, **72**, 991 (1968); J. L. Roark and W. B. Smith, *ibid.*, **73**, 1046 (1969); R. W. Crecey and J. H. Goldstein, *Org. Magn. Resonance*, **2**, 613 (1970). ^c In CDCl₃ solution. ^d In CCl₄ solution. ^e The chemical shift for the methyl protons was 243.3 Hz.

assignments involves a comparison of the substituent effects on the chemical shifts of the F-1 fluorine in **1–3** and **5–7** with the corresponding substituent effects that have been reported⁷ for the series of 4-substituted 1-fluoronaphthalenes **10–15**. This type of effect is conveniently expressed as a substituent chemical shift (SCS), which is defined as the difference between the ¹⁹F chemical shift for the X-substituted compound

(7) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 379 (1967).

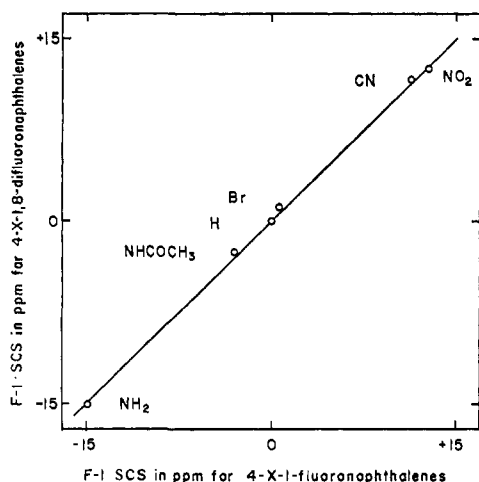
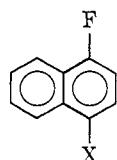


Figure 2. Substituent chemical shift (SCS) values in dimethylformamide solution for the F-1 fluorine in a series of 4-substituted 1,8-difluoronaphthalenes, **1–3** and **5–7**, plotted against SCS values in dimethylformamide solution for the F-1 fluorine in a series of 4-substituted 1-fluoronaphthalenes, **10–15**. The correlation line has been drawn with a slope of unity. The data for **1–3** and **5–7** are given in Table II; the data for **10–15** are taken from ref. 7.



- | | |
|------------|-----------------------------|
| 10, X = H | 13, X = NO ₂ |
| 11, X = Br | 14, X = NH ₂ |
| 12, X = CN | 15, X = NHCOCH ₃ |

and the ¹⁹F chemical shift for the parent compound (with X = H).⁸ The precise linear correlation between the SCS values for the two sets of naphthalene derivatives, which is illustrated graphically in Figure 2, suggests very strongly that the position of the substituent relative to the F-1 fluorine is the same in both series of compounds.

On the basis of all of the cited evidence, there can be no reasonable doubt about the structures of compounds **1–9**.

¹⁹F Nmr Spectra. Figure 3 is a representation of the fluorine nmr spectrum of the nitro compound **5** in dimethylformamide solution as an example of the spectra observed for the series **3–8**. Within each of the four main groups of absorption signals in Figure 3 there is a symmetrical disposition of either eight or four lines around a center position; these four centers are located at 557.3, 482.1, -25.8, and -101.0 Hz relative to the signal from internal 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane. From the spacings and the relative intensities of all of the lines, it appears legitimate to regard these four center positions as an AB quartet for the purpose of evaluating the two fluorine chemical shifts and the F–F coupling constant. In this way, one obtains $\nu_1 = 517.3$ Hz, $\nu_2 = -60.9$ Hz, and $J_{18} = 75.2$ Hz for **5**. The assignment of the lower field chemical shift to F-1 and the higher field chemical shift to F-8 follows from consideration of the different splitting

(8) We adopt the convention⁹ that downfield shifts are positive, which leads to SCS values opposite in sign from those reported earlier by others.⁷

(9) E. F. Mooney, *Org. Magn. Resonance*, **1**, 2 (1969).

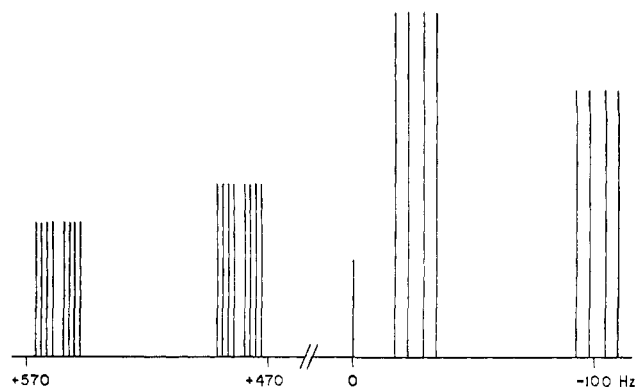


Figure 3. Schematic representation of the ¹⁹F nmr spectrum at 56.4 MHz of 4-nitro-1,8-difluoronaphthalene (**5**) under conditions described in footnote *a* of Table II. Line positions relative to internal 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane are as follows: 566.4, 564.1, 561.9, 559.6, 555.0, 552.7, 550.5, 548.2, 491.2, 488.9, 486.7, 484.4, 479.8, 477.5, 475.3, 473.0, -17.1, -22.5, -29.1, -34.5, -92.3, -97.7, -104.3, and -109.7 Hz.

patterns that occur in the upfield and downfield signals as a consequence of H–F coupling. Thus, the two main signals arising from F-8 should each be split into four lines since F-8 is expected to couple significantly only with H-7 and H-6. However, the two main signals arising from F-1 should each be split into eight lines since F-1 is expected to couple significantly not only with H-2 and H-3 but also with H-5 by way of a “zig-zag” or “W” coupling path.^{4h,10} First-order analysis of the H–F splitting patterns in Figure 3 gives $J_{12} = 11.4$ Hz, $J_{13} = 4.5$ Hz, $J_{15} = 2.3$ Hz, $J_{87} = 12.0$ Hz, and $J_{86} = 5.4$ Hz (see Table I, footnote *b*). The chemical shift assignments for **5** are confirmed by the close correspondence between the SCS value for the low-field signal assigned to F-1 and the SCS value for the F-1 signal from 4-nitro-1-fluoronaphthalene (**13**) as illustrated in Figure 2.

The fluorine spectrum for the amino compound **6** is related to that shown in Figure 3 except that the two eight-line signals assigned to F-1 lie at higher field than the two four-line signals assigned to F-8. Once again, Figure 2 provides confirmation of the chemical shift assignments.

The general features of the fluorine spectra of compounds **3**, **4**, **7**, and **8** are similar to those already described, although some of the signals are broadened, suggesting the importance of additional small long-range H–F couplings in these molecules.

It was not possible to evaluate the F–F coupling constant for the bromo compound **2**, since there was fortuitously so little difference in chemical shift between F-1 and F-8 (even at 94.1 MHz) that the outer lines of the AB quartet pattern were too weak to detect.

Since the fluorines in the parent compound **1** are equivalent by symmetry, it was necessary to evaluate J_{FF} for this compound by an indirect method involving an analysis of the ¹³C satellite peaks in the proton-decoupled ¹⁹F spectrum.¹¹

The parameters of principal interest for the present discussion, the F–F coupling constants, are listed together with the ¹⁹F chemical shifts in Table II.

(10) K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta, Part A*, **23**, 1715 (1967).

(11) We are grateful to Dr. Stanley L. Manatt and coworkers^{4b} for carrying out this measurement for us.

Table II. F-F Coupling Constants and Fluorine Chemical Shifts for Some 4-Substituted 1,8-Difluoronaphthalenes^a

| Compd | Substituent | J_{FF} , Hz ^b | F-1 SCS, ppm | F-8 SCS, ppm |
|-------|---------------------|----------------------------|--------------------|--------------------|
| 1 | H | 58.8 ^c | 0.00 ^d | 0.00 ^d |
| 6 | NH ₂ | 61.8 | -15.02 | -0.13 |
| 4 | CH ₃ | 64.4 ^e | -2.45 | +0.80 |
| 7 | NHCOCH ₃ | 64.6 | -2.55 | +0.30 |
| 8/ | Cl | 65.7 ^f | +0.42 | +1.06 |
| 3 | CN | 65.9 ^h | +11.67 | +2.41 |
| 5 | NO ₂ | 75.2 ⁱ | +12.57 | +2.32 |
| 2 | Br | j | +1.13 ^j | +1.13 ^j |

^a Unless otherwise specified, values refer to measurements at 56.4 MHz of solutions of 0.4 mmol of the indicated compound in 0.4 ml of dimethylformamide. Each reported value of J_{FF} was obtained by averaging peak separations from about six spectra; in no case did the mean deviation exceed 0.3 Hz. To cope with small nonlinearities in sweep, the region of interest on the chart paper was calibrated for each scan by a side-band technique with an audio-oscillator and a frequency counter. Chemical shifts were measured from a single scan in each case; the uncertainty in the derived SCS values is estimated as ± 0.1 ppm. ^b The sign of J_{FF} has been shown to be positive for 1 (see ref 4q and u); the F-F coupling constants for 2-8 are assumed to be positive by analogy. ^c Measured in acetone at 94.1 MHz as described in ref 4n. ^d The signal for 1 is centered 3.40 ppm upfield from that of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as an internal standard. ^e $J = 65.6$ Hz in CCl₄. ^f All values reported for this compound are derived from spectra obtained at 94.1 MHz with a Varian XL-100 spectrometer at Temple University. We are indebted to Professor David R. Dalton and Dr. Ronald Rodebaugh for these measurements. ^g $J = 66.5$ Hz in CCl₄. ^h $J = 66.3$ Hz in acetone, $J = 66.1$ Hz in CDCl₃, and $J = 65.8$ Hz in C₆D₆. ⁱ $J = 75.6$ Hz in acetone. ^j The spectrum of 2 exhibits only one broad multiplet centered at an SCS value of +1.13 ppm. The line width at half-height of about 14 Hz is the same as that for the single broad multiplet in the spectrum of 1. This suggests that F-1 and F-8 in 2 have nearly identical chemical shifts. Because of this fortuitous circumstance, the spectrum of 2 yielded no information regarding J_{FF} . The spectra were similarly uninformative for solutions of 2 in CCl₄, benzene, or acetonitrile.

Electronic Substituent Effects on J_{FF} . It appears from the results given in Table II that the electron-withdrawing or electron-supplying ability of the C-4 substituent, as gauged, for example, either by its Hammett σ_p constant¹² or by the ¹⁹F chemical shift of the F-1 fluorine, does not play a dominant role in determining the magnitude of the F-F coupling constant. Thus, very similar values of J_{FF} , lying within a range of only 1.5 Hz, are obtained for such widely differing substituents as methyl ($\sigma_p = -0.17$), acetamido ($\sigma_p = 0.00$), chloro ($\sigma_p = +0.22$), and cyano ($\sigma_p = +0.66$); furthermore, the values of J_{FF} differ by 9.3 Hz for the similar substituents cyano ($\sigma_p = +0.66$) and nitro ($\sigma_p = +0.78$), and differ by 5.6 Hz for two substituents with identical σ_p constants, hydrogen and acetamido. The lack of a dominant electronic substituent effect is also illustrated graphically in Figure 4, in which values of J_{FF} are plotted against F-1 SCS values. However, one can also argue in favor of a slight dependence of J_{FF} on the electronic character of the substituent by noting that the points for NH₂, NHCOCH₃, CH₃, and Cl in Figure 4 fall close to a line of positive slope, and by asserting that steric factors (see below) cause the points for H, CN, and NO₂ to deviate from that line.

Steric Substituent Effects on J_{FF} . We believe that

(12) (a) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964); (b) P. D. Bolton, K. A. Fleming, and F. M. Hall, *J. Amer. Chem. Soc.*, **94**, 1033 (1972).

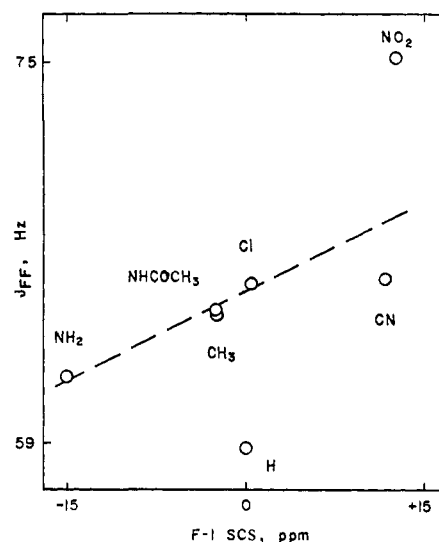


Figure 4. The relationship between J_{FF} and the SCS value for F-1 for a series of 4-substituted 1,8-difluoronaphthalenes. The data are given in Table II.

steric effects represent the primary means by which substituents influence the values of J_{FF} for the compounds listed in Table II. As a means of evaluating the effective size of a C-4 substituent in the 1,8-difluoronaphthalene system, we have calculated the van der Waals repulsion energy that would be associated with the crowding of the substituent against the C-5 hydrogen in the sterically undistorted molecule. For these calculations we have used the Hill equation,¹³ which ex-

$$E = 8.28 \times 10^5 \epsilon e^{-13.59(r/R)} - 2.25 \epsilon (R/r)^6$$

presses the energy, E , of the van der Waals interaction between two nonbonded atoms as a function of their distance of separation, r ,¹⁴ the sum of their van der Waals radii, R , and an energy parameter, ϵ . Table III contains a list of the particular constants that were chosen for use in the calculations; values of bond distances and bond angles for the 1,8-difluoronaphthalenes were assumed by analogy with model compounds. The calculated energies of peri crowding for the C-4 substituents in this system in units of kcal/mol are as follows: 0.2 for H, 0.8 for CN, 1.4 for Cl, 1.9 for CH₃, 2.0 for NH₂ and NHCOCH₃, and 3.0 for NO₂.^{15,16} Some striking similarities can be seen between this pattern of repulsion energies and the pattern of J_{FF} values in Table II. For instance, the compound with the smallest substituent, H, has the smallest J_{FF} , and the compound with the largest substituent, NO₂, has the largest J_{FF} . Furthermore, the calculations indicate that the four substituents whose points fall close

(13) (a) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948); (b) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 449-452.

(14) For calculations involving hydrogen in molecules of type Y-H, we followed the procedure given by N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971), in which the distance r is measured from a point 92% of the way along the Y-H bond instead of directly at the H nucleus.

(15) These values are for the arbitrarily chosen conformations with the substituent planes for NH₂, NHCOCH₃, and NO₂ lying at 45° relative to the ring plane, and the CH₃ group staggered relative to the C-5 hydrogen. The calculated repulsion energies in kcal/mol for some less favorable conformations are as follows: planar NH₂ and NHCOCH₃, 6; planar NO₂, 17; eclipsed CH₃, 10.

(16) Calculations of this type are thought to be reliable within about ± 0.5 kcal/mol.^{13b}

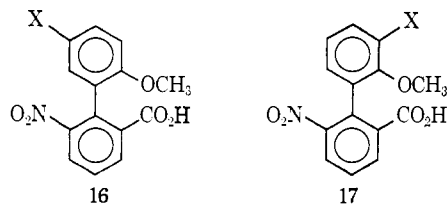
Table III. Assumed Structural Parameters for 4-Substituted 1,8-Difluoronaphthalenes

Bond distances (Å): sp^2 C-H, 1.08;^a sp^2 C-CH₃, 1.51;^a sp^2 C-CN, 1.43;^a sp^2 C-Cl, 1.70;^a sp^2 C-NH₂, 1.41;^{b,c} sp^2 C-NO₂, 1.48;^b methyl C-H, 1.10;^a cyano C≡N, 1.16;^a amino N-H, 1.01;^{a,c} nitro N-O, 1.21^d
 Bond angles: methyl HCH, 109° 28'; cyano CCN, 180°; amino HNH, 112°;^e nitro ONO, 124°^d
 Other parameters: distance between C-4 and C-5, 2.48 Å;^{f-h} bonds from C-4 to X and from C-5 to H presumed parallel; substituent planes for amino^c and nitro^d taken to lie at 45° relative to ring plane.
 van der Waals radii (Å) and Hill equation parameters (ε) in kcal/mol:ⁱ H, 1.50 (0.060);^j sp^3 C, 1.50 (0.116);^k sp C, cyano N, and nitro N, 1.85 (0.033);^l F, 1.35 (0.109);^m Cl, 1.80 (0.314);^m amino N, 1.50 (0.063);^{c,m} nitro O, 1.54 (0.070)ⁿ

^a L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S3s-S23s (1965). ^b T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **18**, 68 (1965). ^c The same value was assumed to apply in a corresponding way for the NHCOCH₃ substituent. ^d J. Trotter, *Acta Crystallogr.*, **12**, 884 (1959); **13**, 95 (1960). ^e V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966). ^f D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960). ^g A. Almenningen, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.*, **14**, 1056 (1961). ^h The carbon skeleton of **1** should not be significantly distorted from that of naphthalene; two fluorines separated by 2.48 Å would experience van der Waals attraction, but this would be counteracted by coulombic repulsion of the two polar CF units. ⁱ Listed values of ε are for interactions between like atoms; for two different interacting atoms, A and B, $\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2}$. ^j N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972). ^k Reference 14. ^l Values assumed to equal those of sp^2 C as given in footnote j. ^m Reference 13b. ⁿ Values assumed to equal those of ketone oxygen as given by N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

to the suggested correlation line in Figure 4 (NH₂, NHCOCH₃, CH₃, and Cl) all have very similar effective size, whereas the two substituents whose points fall below that line (H and CN) are smaller and the substituent whose point falls above that line (NO₂) is larger.

The classical studies of the rates of racemization of optically active biphenyls¹⁷ provide another line of evidence for four of the substituents of interest that their effective sizes are in the sequence H < Cl ~ CH₃ < NO₂. Thus, the ratio of the racemization rate constants for two isomers of types **16** and **17** can be regarded



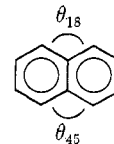
as a measure of the rate-retarding steric buttressing effect of the substituent X, since essentially the same electronic effect¹⁸ should be exerted by X in both isomers. The following are the observed **16/17** rate ratios for racemizations in absolute ethanol at ca. 25° for four different substituents, X: 1.0 for H, 24 for Cl, 29 for CH₃, and 54 for NO₂.¹⁷

Interpretation of Substituent Effects on J_{FF} . We believe that the steric effect described in the preceding section can be accounted for in a straightforward way.

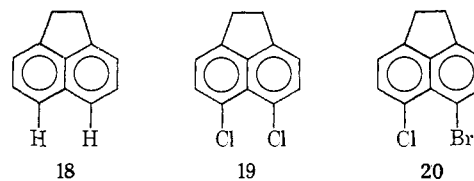
(17) (a) R. W. Stoughton and R. Adams, *J. Amer. Chem. Soc.*, **54**, 4426 (1932); (b) H. C. Yuan and R. Adams, *ibid.*, **54**, 4434 (1932); (c) S. L. Chien and R. Adams, *ibid.*, **56**, 1787 (1934).

(18) These electronic effects are small; for example, the rate for **16** with X = H exceeds that for **16** with X = NO₂ by a factor of only 3.8.

Thus, on the basis of structural studies by X-ray crystallography in the model systems discussed below, it is expected that an increase in the degree of steric crowding between the C-4 substituent and the C-5 hydrogen in the 4-substituted 1,8-difluoronaphthalene system will shorten the distance of separation between the two fluorines¹⁹ and thereby enhance the through-space F-F coupling.^{2,3} In naphthalene itself, the size of the peri CCC angles θ_{18} and θ_{45} has been found to be about 121.5°;²⁰ similar angles have been found for



2-naphthol.²¹ In peri-substituted naphthalenes, the crowding strain leads to an increase in the adjacent peri angle and a decrease in the remote peri angle relative to the angles in naphthalene itself. Three examples of this phenomenon are as follows: in 1,8-bis(phenylethynyl)naphthalene, $\theta_{18} = 125.1^\circ$ and $\theta_{45} = 119.6^\circ$;²² in 1,8-dimethyl-3-bromonaphthalene, $\theta_{18} = 126.8^\circ$ and $\theta_{45} = 117.4^\circ$;²³ and in 1,8-dinitronaphthalene, $\theta_{18} = 130^\circ$ and $\theta_{45} = 112^\circ$.^{24,25} Further evidence that the distortions of the two peri angles in peri-substituted naphthalenes are inversely interrelated comes from the acenaphthene system. Thus, the two-carbon bridge in **18** decreases the peri angle within the five-membered ring to 112.4° and increases the other peri angle to 128.4°;²⁶ other related systems show similar distortions.^{27,28} Finally, the effects of peri crowding also can be seen in the series **18-20**, in which the peri angle



spanned by the two-carbon bridge decreases and the other peri angle increases in response to increasing the

(19) Table III, footnote e.

(20) Table III, footnotes f and g.

(21) H. C. Watson and A. Hargreaves, *Acta Crystallogr.*, **11**, 556 (1958).

(22) A. E. Jungk and G. M. J. Schmidt, *Chem. Ber.*, **104**, 3272 (1971).

(23) M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).

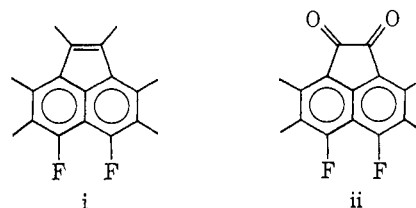
(24) Z. A. Akopyan and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **5**, 496 (1964).

(25) The relative magnitudes of the distortions for the latter two of these three examples further illustrate our contention that peri nitro groups make larger steric demands than peri methyl groups.

(26) H. W. W. Ehrlich, *Acta Crystallogr.*, **10**, 699 (1957).

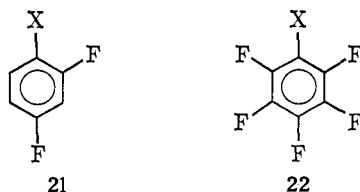
(27) (a) T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **16**, 811 (1963); (b) J. Trotter and T. C. W. Mak, *ibid.*, **16**, 1032 (1963); (c) T. C. W. Mak and J. Trotter, *ibid.*, **17**, 367 (1964).

(28) By recognizing the fact that acenaphthene derivatives have especially large exocyclic peri angles (and hence especially large distances between peri substituents), one can readily explain why such small values of J_{FF} , lying in the range from 29.4 to 35.7 Hz, have been found⁴¹ for molecules of types i and ii.



size of the peri substituents: the angles are 112.4 and 128.4° for **18**,²⁶ 109.8 and 130.9° for **19**,²⁹ and 109 and 138° for **20**.³⁰

We believe that the slight electronic effect discussed above in connection with Figure 4 reflects the electronic influence of the C-4 substituent on a small through-bond component of the overall F-F coupling in the 1,8-difluoronaphthalene system. As model compounds for this through-bond coupling, we have chosen the 1-substituted 2,4-difluorobenzenes **21** and **22**;³¹ thus, in **21** and **22**, as in **1-8**, the two fluorines of interest are



connected by a four-bond pathway involving three intervening aromatic carbons, and the variable substituent is located para to one fluorine and also is conjugated with the other fluorine. For the series of compounds of type **21** with the same set of substituents that are listed in Table II, the values of J_{24} range between -3 and +12 Hz;³² for series **22**, the corresponding values of J_{24} range between -8 and about +8 Hz.³³ If the through-bond contribution to the overall coupling in **1-8** is of similar magnitude,³⁴ then it clearly represents only a small part of the total coupling that ranges between 58.8 and 75.2 Hz in those molecules. Good correlations with positive slopes have been reported between J_{24} and σ_p for series **21**,³² and between J_{24} and the F-4 SCS value for series **22**,³³ which indicates the existence of an electronic substituent effect on the four-bond F-F coupling in these model systems. It is reasonable to suppose that a similar substituent effect exists for the through-bond component of the J_{FF} values listed in Table II, but that this effect is largely masked by the predominance of the through-space component in the 1,8-difluoronaphthalene system; Figure 4 is consistent with this supposition.

In summary, we draw the following three conclusions regarding F-F coupling in the 1,8-difluoronaphthalene system: the coupling occurs predominantly by the through-space mode; a C-4 substituent exerts an important steric effect on the coupling by distorting the molecule in such a way as to influence the F-F distance; and there may be a slight electronic effect of a C-4 substituent on the magnitude of J_{FF} , but it is probably operative on the through-bond component rather than the through-space component of the coupling. Finally, we propose that the earlier generalization^{4h} that through-space F-F coupling might be distinguished

(29) R. L. Avoyan and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **2**, 719 (1961).

(30) R. L. Avoyan and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **5**, 407 (1964).

(31) The large distance between F-2 and F-4 in **21** and **22** precludes any significant through-space interactions.

(32) R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, **90**, 147 (1968).

(33) (a) M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 283 (1969); (b) E. A. Cohen, A. J. R. Bourn, and S. L. Manatt, *J. Magn. Resonance*, **1**, 436 (1969).

(34) The inter-ring through-bond interactions in **1-8** may be even smaller than the intra-ring interactions in **21** and **22**; for example, ${}^3J_{FF} = 4.1$ Hz for 1,5-difluoronaphthalene, whereas ${}^5J_{FF} = 17.7$ Hz for 1,4-difluorobenzene.^{4h}

by its insensitivity to substituents should be modified to allow for steric substituent effects of the type we have described in the preceding discussion.

Experimental Section

Melting points were determined in capillaries in a heated oil bath and are uncorrected. Sublimations were carried out under reduced pressure in a previously described type of apparatus.³⁵ Elemental analyses were performed by M-H-W Laboratories of Garden City, Mich. Unless otherwise specified, nmr spectra were obtained with a Varian A-56/60A spectrometer; sweep widths were calibrated with a Hewlett-Packard 200 ABR audio-oscillator and Beckman 554 F-1 frequency counter. Mass spectra were obtained with a Hitachi-Perkin-Elmer RMS-4 spectrometer combined with a Perkin-Elmer 990 gas chromatograph; the spectra of each of the new compounds described below exhibited parent and fragment ions with the appropriate m/e values.

1,8-Difluoronaphthalene (1). Commercial 1,8-diaminonaphthalene was purified by sublimation at reduced pressure. A mixture of 8.0 g (0.05 mol) of the colorless diamine and 200 ml of aqueous 48% fluoboric acid was stirred magnetically in a hot water bath for 30 min, after which it was cooled to -30° with stirring in a bath of Dry Ice and 2-propanol. An ice-cold solution of 14 g (0.20 mol) of sodium nitrite in 20 ml of water was added dropwise to this mixture during 30 min while the temperature was maintained between -30 and -25°. The solid fluoborate salt was collected on a large sintered glass funnel and was washed with the following series of solvents, each of which had been cooled to -30°: a solution made from 10 ml of aqueous 48% fluoboric acid and 10 ml of water; one 20-ml portion of absolute ethanol; and three 30-ml portions of anhydrous diethyl ether. The resulting light tan solid was dried under reduced pressure in the dark overnight.

The material thus obtained, which amounted to 28 g, was mixed with 50 g of sand in a 500-ml round-bottomed flask equipped with a distilling head, a water-cooled condenser, and a two-necked flask as a receiver that was connected in series to two additional traps. The receiver and the traps were cooled in baths of Dry Ice and 2-propanol. The fluoborate salt was pyrolyzed by careful heating with a free flame. After the exothermic reaction had subsided, the 500-ml flask was heated strongly with the flame in order to distill out any product that might have been trapped in the solid residue. The product was collected by rinsing out the condenser, the receiver, and the traps with diethyl ether. Most of the ether was distilled off through a small distilling head; then 5 ml of 95% ethanol was added and the residual ether was removed by collecting an additional 4 ml of distillate. Water was added to the residue and the product was steam distilled. The solid in the steam distillate was collected on a Büchner funnel and dried in a small-volume desiccator over anhydrous CaSO_4 to give 2.0 g (24%) of a volatile white solid with a strong naphthalene-like odor. A small sample was further purified by several recrystallizations from aqueous ethanol to give **1** as colorless plates with mp 39.4-39.9°. *Anal.* Calcd for $\text{C}_{10}\text{H}_6\text{F}_2$: C, 73.17; H, 3.68. Found: C, 72.97; H, 3.82.

4-Bromo-1,8-difluoronaphthalene (2).³⁶ To a solution of 1.2 g (7.3 mmol) of 1,8-difluoronaphthalene in 3 ml of carbon tetrachloride was added 0.40 ml (1.17 g, 7.3 mmol) of bromine in 1 ml of carbon tetrachloride. A pinch of iron powder was added and the reaction mixture was heated at reflux for 1 hr. The mixture was then cooled and poured through a small column of alumina that was subsequently washed with an additional 50 ml of carbon tetrachloride. The solvent was removed from the eluate by distillation and the residue was steam distilled to give 1.4 g (79%) of a white solid with mp 71-72°. After two recrystallizations of this material from aqueous methanol and a final sublimation under reduced pressure there was obtained a sample of **2** with mp 71.5-73.0°. *Anal.* Calcd for $\text{C}_{10}\text{H}_5\text{F}_2\text{Br}$: C, 49.41; H, 2.07. Found: C, 49.25; H, 1.89.

The 60-MHz proton nmr spectrum³⁷ of **2** in carbon tetrachloride solution showed a one-proton broad doublet at 471 and 479.5 Hz

(35) F. B. Mallory, *J. Chem. Educ.*, **39**, 261 (1962).

(36) For clarity in the discussion, these compounds have been designated as 4-substituted 1,8-difluoronaphthalenes. The systematic names are as follows: **2** is 1-bromo-4,5-difluoronaphthalene; **3** is 4,5-difluoro-1-naphthonitrile; **4** is 4,5-difluoro-1-methylnaphthalene; **5** is 4,5-difluoro-1-nitronaphthalene; **6** is 4,5-difluoro-1-naphthylamine; **7** is *N*-(4,5-difluoro-1-naphthyl)acetamide; and **8** is 1-chloro-4,5-difluoronaphthalene.

(37) See Table I, footnote a.

attributed to H-5 with $J_{56} = 8.5$ Hz, and a four-proton set of signals between 408 and 466 Hz attributed to H-2, H-3, H-6, and H-7.

4-Cyano-1,8-difluoronaphthalene (3).³⁶ A mixture of 243 mg (1.0 mmol) of 4-bromo-1,8-difluoronaphthalene, 90 mg (1.0 mmol) of cuprous cyanide, 5 ml of dimethylformamide, and two drops of pyridine was stirred magnetically and heated at reflux for 4 hr. To the cooled reaction mixture was added 10 g of ice and 10 ml of aqueous 28% ammonia. The resulting tan precipitate was sublimed under reduced pressure to give 127 mg of a white solid, mp 100–116°, that was shown by gas-liquid chromatography to contain some unreacted bromo compound along with the desired cyano compound. These two components were separated by column chromatography on alumina. The bromo compound was eluted from the column first with 60–70° ligroin. Subsequent elution with a 3:1 mixture of 60–70° ligroin and benzene gave the cyano compound; the solid obtained by evaporation of this fraction was recrystallized from 60 to 70° ligroin and finally sublimed under reduced pressure to give colorless crystals of **3** with mp 145.0–145.7°. *Anal.* Calcd for $C_{11}H_8NF_2$: C, 69.84; H, 2.66. Found: C, 69.78; H, 2.49.

4-Methyl-1,8-difluoronaphthalene (4).³⁶ To a solution of 0.50 g (2.1 mmol) of 4-bromo-1,8-difluoronaphthalene in 12 ml of anhydrous diethyl ether was added 2.5 ml (8.2 mmol) of a 21% solution of *n*-butyllithium in hexane. The reaction mixture was maintained under an atmosphere of dry nitrogen and was stirred magnetically. The addition of 0.2 ml (0.29 g, 2.3 mmol) of dimethyl sulfate gave a cloudy mixture that was heated at reflux for 1 hr. The mixture was then diluted with 20 ml of diethyl ether, and 20 ml of aqueous 10% sodium hydroxide was added. The resulting two layers were separated, and the ether layer was washed with water and with saturated aqueous sodium chloride, after which it was dried over anhydrous sodium sulfate. The dried solution was filtered and the solvents were removed with a stream of nitrogen. The residue was chromatographed on alumina with pentane as eluent. The solvent was removed from the appropriate fraction with a stream of nitrogen, and the residue was molecularly distilled to give 0.1 g (27%) of **4** as a colorless oil. This sample of **4** was shown by gas-liquid chromatography to contain a single component, and was characterized by its mass spectrum (parent ion at m/e 178), its ^{19}F nmr spectrum (see Table II and Figure 2), and its proton nmr spectrum. The latter,³⁷ obtained at 60 MHz in carbon tetrachloride solution, showed a one-proton doublet of triplets centered at 451 and 459 Hz attributed to H-5 with $J_{56} = 8$ Hz and $J_{57} = J_{51} = 2$ Hz, a four-proton set of signals between 399 and 444 Hz attributed to H-2, H-3, H-6, and H-7, and a three-proton doublet at 152 and 153 Hz attributed to the C-4 methyl group which is coupled to H-3 with $J = 1$ Hz.

4-Nitro-1,8-difluoronaphthalene (5).³⁶ A solution of 400 mg (2.4 mmol) of 1,8-difluoronaphthalene, 1.6 ml of glacial acetic acid, and 1.1 ml (1.6 g, 25 mmol) of fuming nitric acid was heated on a steam bath for 4 hr, after which it was cooled and poured onto 10 g of crushed ice. The resulting yellow solid was purified by sublimation under reduced pressure and recrystallization from 95% ethanol to give 390 mg (77%) of yellow needles with mp 125.0–126.3°. Two more recrystallizations from 95% ethanol gave a sample of **5** with mp 126.3–126.6°. *Anal.* Calcd for $C_{10}H_8NO_2F_2$: C, 57.43; H, 2.41. Found: C, 57.15; H, 2.35.

4-Amino-1,8-difluoronaphthalene (6).³⁶ To a mixture of 2.5 g (0.012 mol) of 4-nitro-1,8-difluoronaphthalene, 40 ml of 95% ethanol, and 2.5 ml of concentrated aqueous HCl was added 2.5 g (0.045 mol) of iron powder in five portions over a period of 20 min. The mixture was then heated at reflux for 2 hr, after which it was made basic with ethanolic NaOH and filtered. The brown solid was digested twice with hot 95% ethanol and the combined filtrates were evaporated to dryness under reduced pressure. The residual dark solid was sublimed under reduced pressure to give 1.5 g (70%)

of a colorless sample of **6** with mp 100–102°. *Anal.* Calcd for $C_{10}H_8NF_2$: C, 67.09; H, 3.94. Found: C, 66.89; H, 3.86.

The 60-MHz proton nmr spectrum³⁷ of **6** in carbon tetrachloride solution showed a broad two-proton signal at 228 Hz attributed to the amino group and a five-proton set of signals between 386 and 452 Hz attributed to the aromatic protons.

4-Acetamido-1,8-difluoronaphthalene (7).³⁶ A solution of 400 mg (2.2 mmol) of 4-amino-1,8-difluoronaphthalene, 0.21 ml (227 mg, 2.2 mmol) of acetic anhydride, and 8 ml of glacial acetic acid was heated on a steam bath for 1 hr. The reaction mixture was then diluted while hot with 10 ml of water and cooled in an ice bath. The crystalline precipitate was collected and sublimed under reduced pressure to give 410 mg (83%) of white solid with mp 198.0–198.8°. Recrystallization from methanol followed by sublimation under reduced pressure gave a sample of **7** with mp 198.8–199.2°. *Anal.* Calcd for $C_{12}H_9NOF_2$: C, 65.15; H, 4.10. Found: C, 65.00; H, 3.95.

4-Chloro-1,8-difluoronaphthalene (8).³⁶ A mixture of 700 mg (3.9 mmol) of 4-amino-1,8-difluoronaphthalene, 3 ml of concentrated aqueous HCl, and 3 ml of water was maintained at 0° while a solution of 270 mg (3.9 mmol) of sodium nitrite in 2 ml of water was added dropwise. The resulting solution of the diazonium ion was added to 4 ml of a solution containing 6 mmol of freshly prepared⁸⁸ cuprous chloride in concentrated aqueous HCl. The mixture was stirred magnetically at room temperature until gas evolution had ceased, and was then heated on a steam bath for 15 min. Steam distillation of the reaction mixture gave 650 mg (84%) of the product as a white solid with mp 87.5–90.0°. This material was purified by column chromatography on alumina with 60–70° ligroin as eluent and subsequently by sublimation under reduced pressure to give a sample of **8** with mp 90.2–91.4°. *Anal.* Calcd for $C_{10}H_8F_2Cl$: C, 60.48; H, 2.54. Found: C, 60.23; H, 2.27.

The 60-MHz proton nmr spectrum³⁷ of **8** in carbon tetrachloride solution showed a one-proton doublet of triplets centered at 472.5 and 481 Hz attributed to H-5 with $J_{56} = 8.5$ Hz and $J_{57} = J_{51} = 1.5$ Hz, and a four-proton set of signals between 411 and 460 Hz attributed to H-2, H-3, H-6, and H-7.

5-Fluoro-4-methoxy-1-nitronaphthalene (9). A solution of 209 mg (1.0 mmol) of 4-nitro-1,8-difluoronaphthalene (**5**) and 60 mg (1.1 mmol) of sodium methoxide in 8 ml of anhydrous methanol was heated at reflux for 1 hr. The solution was allowed to stand overnight at room temperature, after which the solvent was evaporated under reduced pressure. The residue was sublimed under reduced pressure to give 165 mg (75%) of material with mp 94.5–96.0°. Two recrystallizations of this product from 95% ethanol gave a sample of **9** as yellow needles with mp 96.7–97.2°. *Anal.* Calcd for $C_{11}H_8NO_3F$: C, 59.73; H, 3.65. Found: C, 59.47; H, 3.40.

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(38) C. S. Marvel and S. M. McElvain, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 170.