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Fluorine Magnetic Resonance Studies. VII* Fluorine–Fluorine Coupling Over Five Bonds in 1-Fluoro-2-(2′-fluorophenyl)ethanes

David A. Burgess, Michael F. Finn, David Jordan,
Ian D. Rae and Barry D. Walters

Chemistry Department, Monash University,
Clayton, Vic. 3168.

Abstract

Spin–spin coupling between an aromatic fluorine and fluorines in an adjacent side chain (Ar–C–C–F), with J values in the range 2–5 Hz, is reported for four new compounds. The coupling probably arises from through-space interactions taking place when rotation of the side chain brings the two types of fluorine into close proximity. In a Diels–Alder adduct of fluoranil and 1-fluoro-4-methylanthracene, this proximity is denied the fluorines and no coupling is observed.

Introduction

In a recent paper,[1] we reported fluorine–fluorine spin–spin coupling over four bonds in a number of fluoro(2′-fluorophenyl)methanes. The coupling was largely of the through-space type, falling off rapidly as the distance between the aromatic and aliphatic fluorines increased. The size of the coupling also depended on the number of aliphatic fluorines, being larger for the fluorines of CF_3 groups than for CF_2 and CF groups, respectively.

Contemplating extension of this work, we have examined a few 1-fluoro-2-(2′-fluorophenyl)ethanes, and find that fluorine–fluorine coupling over five bonds ($^5J_{FF}$) is often observed. We presume that through-space mechanisms are also responsible here but we have decided not to pursue the work, and report here the results of our brief study.

Results and Discussion

The fluoromethyl (1), difluoromethyl (2) and trifluoromethyl (3) compounds show quite appreciable fluorine–fluorine coupling over five bonds. For through-space coupling to be effective, conformations such as (4), which bring the fluorines close together, would need to be populated to some extent.

Examples are known of coupling between the fluorines of adjacent CF groups on aromatic rings,[2] and also for *o*-fluorines and fluorines attached to a two-carbon

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* Part VI, *Aust. J. Chem.*, 1984, **37**, 1437.

[1] Rae, I. D., Burgess, D. A., Bombaci, S., Baron, M. L., and Woolcock, M. L., *Aust. J. Chem.*, 1984, **37**, 1437.

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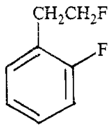
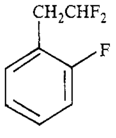
side chain.[3–6] The couplings are shown with formulae (6)–(11), and we see that they are so large that our values should not occasion any surprise. We know that when a conformation such as (4) is strictly enforced on the molecule, e.g., in the case of 4,5-difluorophenanthrenes, then $^5J_{FF}$ is about 170 Hz,[7] and that even a larger coupling is observed in compound (12) which may be assumed to have the conformation shown.[8] Given such prodigious values, the 'proximate' conformation (4) need make only a very minor contribution for couplings of a few hertz to be observed.



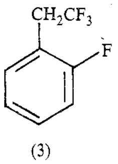
(1)

$^5J_{FF}$ 2·3 Hz



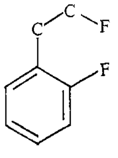
(2)

$^5J_{FF}$ 2·8 Hz

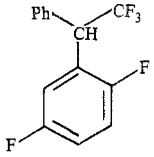


(3)

$^5J_{FF}$ 5·0 Hz

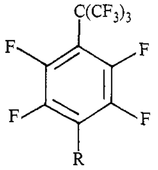


(4)



(5)

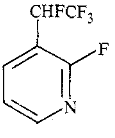
$^5J_{FF}$ 3·1 Hz



(6)

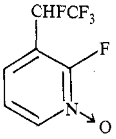
$^5J_{FF}$ 26 Hz

(four examples)



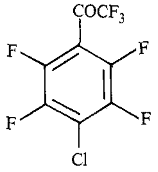
(7)

$^5J_{FF}$ 6·7 Hz



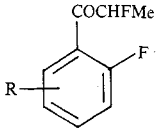
(8)

$^5J_{FF}$ 13·0 Hz



(9)

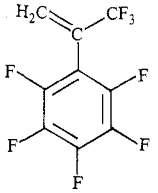
$^5J_{FF}$ 11·1 Hz



(10)

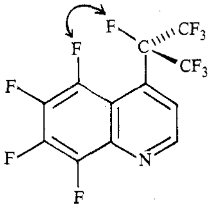
$^5J_{FF}$ 13·0–17·0 Hz

(several examples)



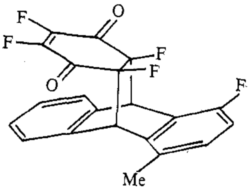
(11)

$^5J_{FF}$ 6·8 Hz

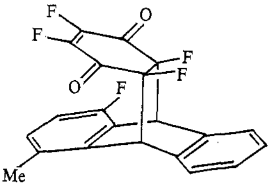


(12)

$^5J_{FF}$ 196·4 Hz



(13)



(14)

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An interesting test of this theory would be to examine the spectra of compounds in which the aliphatic fluorine could never approach the aromatic one, for example if the 'side chain' were part of a ring fused to the aromatic ring. Indeed, the literature does contain a few examples of fluorinated dihydronaphthalene ring systems which meet this condition,[9] but the absence of $^{5}J_{FF}$ in the reported data was not, alone, strong evidence that coupling did not exist. Accordingly, we synthesized the Diels–Alder adducts (13) and (14), in the former of which the fluorines, although separated by five bonds, would not be all that far apart in space although the bond pathway is nothing like coplanar.

1-Fluoro-4-methylanthracene was prepared from the known 9,10-dione by reduction with zinc.[10] An interesting $^{5}J_{FH}$ in this anthracene (1·8 Hz) was established when the C 10 *meso* hydrogen was clearly identified by means of a nuclear Overhauser experiment involving the methyl hydrogens. Heating 1-fluoro-4-methylanthracene with an equimolar amount of 2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione (fluoranil) in solvents such as benzene gave a deep blue charge-transfer complex. When the mixture of the anthracene and fluoranil was heated for a few minutes, the adducts (13) and (14) were formed, as evidenced by the observation of a peak at *m/z* 390 in the mass spectrum of the mixture. Thin-layer chromatography and n.m.r. spectroscopy showed that the mixture contained the two adducts in about equal amounts along with some quantities of each starting material. Attempts to isolate the adducts failed because of their facile reversion to the anthracene and fluoranil, so we believe that we were working with an equilibrium mixture in which the equilibrium was rapidly established in solution.[11] The ^{19}F n.m.r. spectra, reported in the Experimental, showed no sign of coupling between the aromatic and aliphatic fluorines in either isomer.

Experimental

Instrumentation was as described in Part VI.[1]

1-Fluoro-2-(2′-fluorophenyl)ethane (1)

2-(2′-Fluorophenyl)ethanol[12] (1·0 g) was allowed to react with SF_4 and pyridine in a mixture of carbon tetrachloride and cyclohexane in a stainless steel reaction vessel as described by Schaefer.[13] The crude, neutral product was purified by gas–liquid chromatography to give *1-fluoro-2-(2′-fluorophenyl)ethane* as a colourless oil in 57% yield (Found: C, 67·7; H, 5·8. $C_8H_8F_2$ requires C, 67·6; H, 5·7%). ^{1}H n.m.r. δ 3·06, dtd, J 22·1, 6·6, 1·1 Hz, CH_2; 4·60, dtd, J 46·8, 6·6, approx. 0·5 Hz, CH_2F; 6·8–7·4, m, 4ArH. ^{19}F n.m.r. δ 216·67, d, J 2·3 Hz, CH_2F; 119·10, d, J 2·3 Hz, F 2′.

1,1-Difluoro-2-(2′-fluorophenyl)ethane (2)

1,1-Difluoro-2-(2′-fluorophenyl)ethene[14] (2·0 g) was dissolved in ethanol (40 ml), and reduced with hydrogen at 3 atm pressure over Pd–C catalyst (30% Pd, 40 mg). Isolation of the crude product

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and purification by gas–liquid chromatography gave *1,1-difluoro-2-(2′-fluorophenyl)ethane* as a colourless liquid in 96% yield (Found: C, 60·0; H, 4·4. $C_8H_7F_3$ requires C, 60·0; H, 4·4%). ^{1}H n.m.r. δ 3·19, ttd, J 16·3, 4·7, 1·3 Hz, CH_2; 5·95, ttd, J 56·3, 4·7, 0·6 Hz, CH; 6·9–7·4, m, 4ArH. ^{19}F n.m.r. δ 113·08, d, J 2·8 Hz, CHF_2; 116·11, t, J 2·8 Hz, F2′.

1,1,1-Trifluoro-2-(2′-fluorophenyl)ethane (*3*)

(2′-Fluorophenyl)acetic acid[15] (2·0 g) was allowed to react with SF_4 (approx. 3 equiv.) in a stainless steel reaction vessel for 14 h at 160°. The neutral product was isolated and purified by gas–liquid chromatography to give *1,1,1-trifluoro-2-(2′-fluorophenyl)ethane* as a colourless liquid in 42% yield (Found: C, 54·1; H, 3·6. $C_8H_6F_4$ requires C, 53·9; H, 3·4%). ^{1}H n.m.r. δ 3·45, qd, J 10·5, 1·0 Hz, CH_2; 6·7–7·6, m, 4ArH. ^{19}F n.m.r. δ 66·54, d, J 5·0 Hz, CF_3; 117·47, q, J 5·0 Hz, F2′.

2-(2′,5′-Difluorophenyl)-1,1,1-trifluoro-2-phenylethane (*5*)

Sodium borohydride (0·79 g, 19·2 mmol) in 0·2 M aqueous sodium hydroxide (10 ml) was added dropwise over 45 min to a solution of 2,2,2-trifluoroacetophenone (1·0 g, 5·75 mmol) in methanol (10 ml) which was stirred at 18–25°. After a further 15 min, the methanol was removed under reduced pressure, and the residue partitioned between water and diethyl ether (30 ml). The ether solution was washed with water, dried ($MgSO_4$), and evaporated to give the secondary alcohol as a yellowish liquid (0·73 g, 72% yield). Infrared: ν_{max} 3400 cm^{-1}. ^{1}H n.m.r. δ 3·72, s, OH; 4·92, q, J 7 Hz, CH; 7·28, s, 5ArH. This alcohol (0·6 g, 3·45 mmol), *p*-difluorobenzene (3·9 g, 34·5 mmol) and aluminium chloride (0·46 g, 3·46 mmol) were mixed together and stirred at 50–60° for 5 h. The mixture was poured onto ice and extracted with diethyl ether (30 ml), and the ether solution washed with water and dried over $MgSO_4$. The ether and excess difluorobenzene were removed under reduced pressure to give the crude product as an oil (0·38 g, 41% yield). A pure sample of the liquid *2-(2′,5′-difluorophenyl)-1,1,1-trifluoro-2-phenylethane* was separated by preparative gas chromatography (Found: C, 61·7; H, 3·6. $C_{14}H_9F_5$ requires C, 61·8; H, 3·3%). ^{19}F n.m.r. δ 66·6, d, J 3·1, CF_3; 118·0, q, J 17·2, 3·1 Hz, F2′; 123·2, d, J 17·2 Hz, F5′.

1-Fluoro-4-methylanthracene

1-Fluoro-4-methyl-9,10-dihydroanthracene-9,10-dione[16] (6·49 g), zinc dust (28·2 g), copper sulfate (0·2 g) and 17% ammonia solution (300 ml) were stirred at 70° for 4 h as described by Roberts and Yaveri.[10] The organic product was recovered and purified by crystallization from propanol and conc. HCl at 0° to give *1-fluoro-4-methylanthracene* (3·49 g, 61% yield), m.p. 36–39°. The material could also be produced by reduction of the dione with zinc in pyridine/80% acetic acid. Chromatography on alumina, eluting with hexane, and subsequent recrystallization from hexane gave an analytical sample, m.p. 44·5–46° (Found: *m/z* for molecular ion, 210·0845. $C_{15}H_{11}F$ requires 210·0845). ^{1}H n.m.r. δ 2·75, narrow m, CH_3; 6·98, dd, J 7·6, 10·6 Hz, H2; 7·10, br d, J 8 Hz, H3; 7·48, m, H6,7; 8·02, m, H5,8; 8·45, d, $^5J_{HF}$ 1·8 Hz, H10; 8·65, s, H9. The assignment of H10 was made by irradiation at the CH_3 resonance frequency, whereupon a 10% Overhauser enhancement of the δ 8·45 signal was observed. ^{19}F n.m.r. δ 125·99, s (^{1}H-decoupled). U.v. spectrum: λ_{max} (EtOH) 365 (ε 3500), 356 (4180), 345 (3180), 328 (2230), 314 (1730), 252 nm (85520).

Diels–Alder Adducts (*13*) *and* (*14*) (*2,3,4a,5,9a-Pentafluoro-8-methyl-1,4,4a,9,9a,10-hexahydro-9,10[1′,2′]-benzenoanthracene-1,4-dione Isomers*)

Fluoranil (0·54 g, 3·0 mmol) and 1-fluoro-4-methylanthracene (0·084 g, 0·4 mmol) were mixed thoroughly and heated to 120° (oil bath) in an unstoppered flask until sublimation of fluoranil into the cooler part of the flask had apparently ceased. The mass spectrum of the residue showed peaks at *m/z* 390 (adducts), 210 [fluoro(methyl)anthracene] and 180 (fluoranil). As well as some fluoranil, the residue contained two adducts in ratio 55 : 45. Major adduct: ^{19}F n.m.r. δ (CD_3COCD_3)

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123·9, s, ArF; 134·8, narrow AB pattern, *J* approx. 8 Hz, 2 =CF; 159·2, d, *J* 18 Hz, CF; 159·8, d, *J* 18 Hz, CF. Minor adduct: ^{19}F n.m.r. δ (CD_3COCD_3) 127·2, s, ArF; 135·5, s, 2 =CF; 160·8, d, *J* 18 Hz, CF; 161·4, d, *J* 18 Hz, CF.

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