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LONG-RANGE $^{13}C_{sp^2}$-^{19}F SPIN-SPIN COUPLINGS IN MONOFLUORO[2.2]CYCLOPHANES

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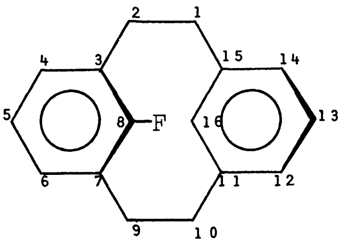
The title couplings are observed in 8-fluoro[2.2]metacyclophane, 1, and 8-fluofo[2.2]metaparacyclophane, 2, but not in 4-fluoro[2.2]-paracyclophane, 3.

Although steric proximity of non-bonded atoms has been well known as an important factor in determining chemical shifts of the atoms, much less is known its effect to cause long-range spin-spin couplings between the atoms.[1,2] This is especially true of long-range $^{13}C_{sp^2}$ spin interactions with fluorine.

In order to explore this type of $^{13}C_{sp^2}$-^{19}F couplings, we have studied ^{13}C NMR spectra[3] of monofluoro[2.2]cyclophanes, 1 - 3,[4] in which the fluorine is close in space to one or two of the opposite aryl carbons (C-16 in 1, C-15 and -16 in 2, and C-13 in 3). In these compounds, couplings via interaction between the 2p-orbitals of those atoms (in 1 and 2 but not in 3) and/or π-π interaction (in 1 - 3)(see 4) may be potentially available, but a hyperconjugation route would be less available because of the practically perpendicular orientation of the C-F bond to the 2p-orbital of the carbon under consideration. In the present work, the ^{13}C-^{19}F couplings were determined by direct measurement of the splitting in each of the ^{13}C signals. Table 1 gives the chemical shifts and coupling constants obtained. The data show that long-range coupling is significant in 1 (for C-16 only) and 2 (for C-15 and -16) and that the 2p-2p and/or π-π interaction is apparently operating here. In view of the fact[5] that no coupling is observed in 3, the couplings seem due predominantly to the 2p-2p interaction. This explanation is supported by the following results of ^1H-^{19}F couplings: in 1 and 2, no coupling from ^{19}F to ^1H attached to the ^{19}F-coupling carbon is observed. In 3, the ^1H spectrum is so complicated that a coupling between ^{19}F and ^1H-13 can not be confirmed, but the presence of this coupling may be expected from the fact that similar couplings are observed in 4,5,7,8-tetrafluoro[2.2]paracyclophane.[1a]



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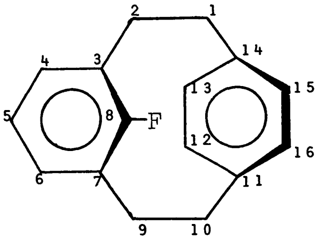

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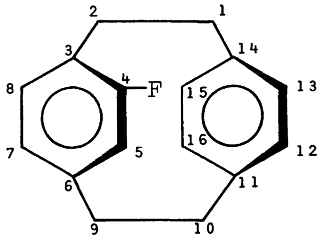

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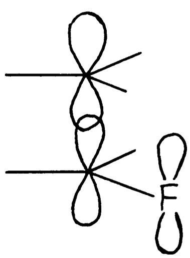

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Table 1. ^{13}C Chemical Shifts (δ)[a] and ^{13}C-^{19}F Coupling Constants (Hz)

Carbon number	1		2		3	
	δ_C	J_{CF}	δ_C	J_{CF}	δ_C	J_{CF}
1	40.8	0.0	37.4	0.0	34.3^{d}	0.0
2	33.7	0.0	27.9	0.0	30.1	0.0
3	128.7	18.3	128.9	19.5	125.8	18.3
4	127.4	4.9	128.1	4.9	161.1	245.4
5	125.0	4.9	123.0	3.7	122.2	22.0
6	127.4	4.9	128.1	4.9	142.8	7.3
7	128.7	18.3	128.9	19.5	128.0	2.4
8	162.2	248.4	161.3	246.6	135.4	6.1
9	33.7	0.0	27.9	0.0	34.8^{d}	0.0
10	40.8	0.0	37.4	0.0	35.3^{d}	0.0
11	138.4	0.0	137.1	0.0	138.8^{e}	0.0
12	126.0	0.0	126.9^{c}	0.0	132.9^{f}	0.0
13	128.4	0.0	126.9^{c}	0.0	129.2^{b}	0.0
14	126.0	0.0	137.1	0.0	139.7^{e}	0.0
15	138.4	0.0	130.5^{c}	4.9	132.5^{f}	0.0
16	131.4^{c}	3.7	130.5^{c}	4.9	133.5^{f}	0.0

[a] Chemical shifts were assigned on the basis of the ^{1}H off-resonance decouplings, additivity parameters, and coupling patterns, unless otherwise noted. [b] Pseudo-geminal substituent effect.5) [c] Assigned by ^{1}H selective decouplings using the ^{1}H data: δ = 4.30 for H-16 in 1, and 5.80 for H-12 (-13) and 7.04 for H-15 (-16) in 2. [d,e,f] Assignments may be reversed.

References and Notes

1) For long-range ^{1}H-^{19}F couplings, see (a) R. Filler and E. W. Choe, J. Amer. Chem. Soc., 91, 1862 (1969); (b) M. S. Newman, R. G. Mentzer, and G. Slomp, ibid., 85, 4018 (1963); K. L. Servis and F. R. Jerome, ibid., 93, 1535 (1971); F. Vögtle and P. Neumann, Tetrahedron, 26, 5255 (1970). For long-range ^{13}C-^{19}F couplings, see Ref.2.

2) F. R. Jerome and K. L. Servis, J. Amer. Chem. Soc., 94, 5896 (1972).

3) ^{13}C and ^{1}H NMR(FT) spectra were measured for ca.0.2 M solutions in $CDCl_3$ using a JEOL PFT-100 spectrometer operating at 25.03 and 99.53 MHz, respectively. The ^{13}C measurement conditions were: data points, 8192; accumulation number, 2000 - 3600; spectral width, 5 kHz; pulse width, 8 μsec (45°); repetition time, 3 sec; spinning tube of 10 mm diameter.

4) Compounds 1 and 2, known substances, were prepared by the methods reported: F. Vögtle, Angew. Chem. internat. Edit., 8, 274 (1969); V. Boekelheide, P. H. Anderson, and T. A. Hylton, J. Amer. Chem. Soc., 96, 1588 (1974). 3, a new compound, was prepared in a similar manner and identified by its mass and ^{1}H and ^{13}C NMR spectra and by its elemental analysis; mp. 233 - 234°C.

5) This agrees with the recent result that in 4-acetyl[2.2]paracyclophane no coupling is observed between the carbonyl and the opposite aryl carbons: J Marshall, L. G. Faehl, and N. D. Ledford, Spectroscopy Lett., 9, 877 (1976).

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