lution. The spectra of the silver(I) complexes also show that exchange reactions are slow [e.g., observation of $^{1}J(^{15}N-^{107,109}Ag)$ and $^{3}J(^{1}H-^{107,109}Ag)$], and this is surprising because, as mentioned before, silver(I) complexes are prone to intermolecular exchange reactions.[11b] However, during the detailed $^{1}H-^{1}H$ decoupling and NOE difference experiments of complex **2a** at room temperature for establishing the assignment of the A and B site pyridine imine protons, an A $\rightleftarrows$ B site exchange was observed. A study on the mechanism of this process which is apparently dependent on the metal centers [Ag(I) or Cu(I)] and on the 6-R (R = H or Me) substituents is in progress.[31]

Conclusions

The silver(I) and copper(I) complexes of the N_4 ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy have similar $[M_2(N_4)_2]^{2+}(O_3SCF_3)_2^-$ structures in the solid and in solution, showing that the study of Ag(I) complexes as models of the corresponding Cu(I) complexes is feasible.

This paper shows for the first time that by using multinuclear NMR techniques (natural abundance ^{15}N and ^{109}Ag NMR) subtle differences in metal–ligand bond lengths, as found in the solid, can be detected in the solution structures of rather complex metal–polydentate ligand complexes. This result is of significance for future studies of structural and bonding features, not only in the coordination chemistry of metal 1B complexes but also in the field of biological copper-containing macromolecules when the Cu(I) ions can be replaced by Ag(I).[32]

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Registry No. **1a**, 90605-88-2; **1b**, 90605-89-3; **2a**, 76317-71-0; **2b**, 76317-73-2; **3a**, 76317-75-4; **3b**, 90605-91-7; ^{13}C, 14762-74-4; ^{15}N, 14390-96-6; ^{107}Ag, 14378-37-1; ^{109}Ag, 14378-38-2; (*R*,*S*)-1,2-diaminocyclohexane, 1436-59-5; pyridine-2-carbaldehyde, 1121-60-4; 6-methylpyridine-2-carbaldehyde, 1122-72-1.

Supplementary Material Available: Listing of positional and thermal parameters for all atoms of **2a** (Table I), IR data of **2** and **3** (Table SI), bond lengths and bond angles of **2a** (Table SII), and listings of observed and calculated structure factors of **2a** (27 pages). Ordering information is given an any current masthead page.

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Preparation and ^{13}C NMR Spectroscopic Study of Fluoroadamantanes and Fluorodiamantanes: Study of $^{13}C-^{19}F$ NMR Coupling Constants

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Abstract: In mono-, di-, tri-, and tetrafluoroadamantanes the effect of progressive addition of fluorine on the ^{13}C chemical shifts and $^{n}J_{CF}$ values were studied. Specific trends in both these values were shown. A series of monofluorodiamantanes and difluorodiamantanes were also prepared. SCS (substituent effect on ^{13}C chemical shifts) and $^{n}J_{CF}$ values were analyzed on the basis of the type and the number of gauche interactions in the system. Fluorine–fluorine coupling constants and ^{13}C isotope induced fluorine chemical shift differences in the polyfluoro compounds were calculated by spin simulation technique and analyzed.

Structural ^{13}C NMR spectroscopic studies generally focus on ^{13}C NMR chemical shifts (δ_C) or $^{13}C-^{1}H$ coupling constants (J_{CH}). Applications are, for the most part, based on empirical correlations of ^{13}C shieldings or J_{CH} values and molecular geometry.[1-3] Empirical correlations of substituent effects on ^{13}C chemical shifts (SCS) have also been studied in recent years.[4]

There is continuing interest in spin–spin coupling between different nuclei and the factors that influence this phenomenon. Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory[5] that coupling via electrons originates from three types of interaction between the magnetic moments due to the nuclear spin and the electrons. The three types are (a) orbital interaction with the magnetic field due to the orbital motion of electrons, (b) dipolar interaction with the electron spin, and (c) Fermi contact interaction with the electron spin. While these three contributions may vary in sign as well as in magnitude, calculations indicate that coupling between the majority of first-row elements is dominated by the Fermi contact[6-12] and,

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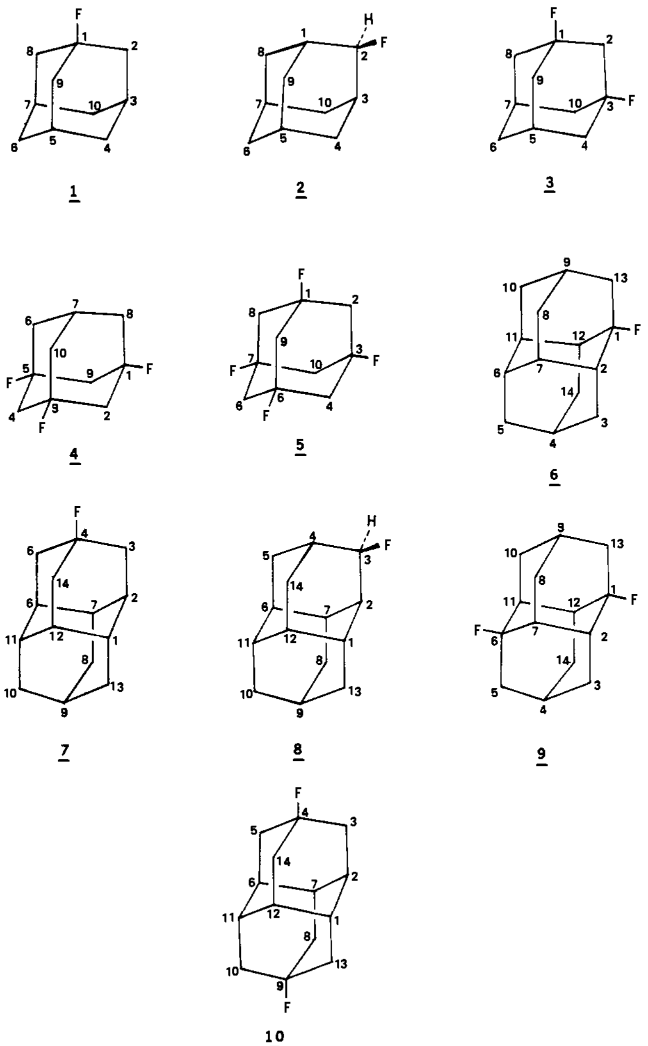
Table I. Preparation of Fluoroadamantanes and -diamantanes in $NO_2^+BF_4^-$/PPHF

compd	starting halide	halide: $NO_2^+BF_4^-$	reaction time/temp, °C	% yield	mp,[b] °C	lit. mp or elemental analysis[c]
1[29]	bromide	1:1.5	3 h/rt[d]	96	225	225–227[52]
2	*a*		3 h/rt[d]	88	254–255	254[53]
3	chloride	1:3	15 h/50	85	239	240–241[54]
4	bromide	1:4.5	5 days/50	89	243	244–245[54]
5	bromide	1:6	7 days/50	86	232	252[54]
6[29]	bromide	1:1.5	10 h/rt[d]	95	245	C, 81.3 (81.5); H, 9.1 (9.3); F, 9.6 (9.2)
7	*a*		4 h/rt[d]	90	218–220	C, 81.4 (81.5); H, 8.9 (9.3); F, 9.6 (9.2)
8	*a*		6 h/rt[d]	90	223	C, 81.6 (81.5); H, 9.3 (9.3); F, 8.7 (9.2)
9	bromide	1:3	24 h/50	95	284	C, 74.9 (75.0); H, 8.2 (8.1); F, 16.9 (16.9)
10	chloride	1:3	15 h/50	86	271–273	C, 74.8 (75.0); H, 8.2 (8.1); F, 16.6 (16.9)

[a] Starting material is the corresponding alcohol and PPHF was used as the reagent and solvent. [b] All melting points are measured in sealed capillary and are uncorrected. [c] Observed percentage (values in parentheses are calculated percentages). [d] rt = room temperature.

Chart I



1 **2** **3** **4** **5** **6** **7** **8** **9** **10**

as a result, would be expected to correlate with the product of the s electron densities at the coupled nuclei. These predictions are supported by experimental observations.[9-11] However, despite successful applications of the theory, using only the Fermi contact term, to C–H coupling[13] and, to a lesser extent, C–C coupling[8,14] similar theoretical evaluations of C–F couplings are less than satisfactory.[14] Calculational approaches that have included the orbital and dipolar interactions show the importance of these contributions to C–F and F–F couplings, but the calculations are still far from accurate in reproducing experimental J_{CF} values.[6,15-18] Some lack of accuracy may be attributed to the limitations imposed by the inadequacies of approximate wave functions. Thus, there has been considerable effort to provide experimental values of $^nJ_{CF}$[1,9-11,19-21] and to find empirical correlations with other molecular properties that are dependent on the same electronic characteristics of the molecules. Recently Della et al.[22] reported the carbon–fluorine spin coupling constants in a series of polycyclic bridgehead fluorides. They showed that the magnitude of $^1J_{CF}$ in such structurally similar compounds is determined by Fermi contact but only because the noncontact terms (dipolar and orbital contribution), while significant, are relatively constant in their case. Olah et al.[23] on the basis of a study of C–F couplings in carbocationic systems (fluorine-substituted aryl carbenium ions) demonstrated that the dominent influence on $^1J_{CF}$ in structurally similar compounds is the extent of resonance interaction of fluorine lone pair with the π system. Thus, such experimental data of $^nJ_{CF}$ values have proven to be of at least some assitance toward a better understanding of the coupling phenomenon.

Interested in the study of adamantanoid hydrocarbons, we recently reported[24] one-bond ^{13}C–^{13}C coupling constants, using the INADEQUATE pulse sequence technique,[25] in a variety of 1- and 2-substituted adamantanes and 2,2-disubstituted adamantanes. Adamantane derivatives are one of the most suitable model compounds for such investigations as they possess a rigid framework and well-defined geometries. Recently Duddeck et al.[26] have studied the substituent effects on the ^{13}C chemical shifts

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of substituted adamantanes, diamantanes, and triamantanes.

Results and Discussion

In continuation of our studies on adamantanoid hydrocarbon, we wish to report the preparation of a series of bridgehead mono- and polyfluorinated adamantanes and diamantanes, and their ^{13}C and ^{19}F NMR spectroscopic study with emphasis on $^{n}J_{CF}$ coupling constants (observed from the ^{13}C spectra).

Preparation. The simplest procedure for the preparation of organofluorides involves halogen exchange using hydrogen fluoride.[27] As this method involves use of volatile, highly corrosive anhydrous hydrogen fluoride, to overcome these difficulties we have introduced pyridine polyhydrogen fluoride (PPHF), as a convenient fluorinating agent.[28] This reagent, however, was found to be unsuitable to convert tertiary adamantanoid halides to their corresponding fluorides.

Recently we reported[29] the conversion of 1-bromoadamantane and 1-bromodiamantane to the corresponding fluorides in excellent yields using $NO_2^+BF_4^-$/PPHF reagent. The ease of this conversion of monobromides to monofluorides prompted us to investigate the preparation of a series of di- and trifluorinated adamantanes and diamantanes starting from the corresponding bromides or chlorides. The fluorides **1–10** (cf. Chart I), except **2**, **7**, and **8**, were prepared using the $NO_2^+BF_4^-$/PPHF reagent.

The corresponding bridgehead bromo- or chloroadamantanes and bromo- and chlorodiamantanes were prepared from the parent hydrocarbons by using literature procedures.[30,31] Reaction of the halides with $NO_2^+BF_4^-$/PPHF gave the corresponding fluorides in good to excellent yields (see Experimental Section and Table I for details). The secondary fluorides **2** and **8** and the bridgehead fluoride **7** were prepared from their corresponding alcohols in PPHF.[28]

Nuclear Magnetic Resonance Studies. The ^{13}C and ^{19}F NMR chemical shifts of the fluoroadamantanes and -diamantanes are listed in Tables II and III, along with ^{13}C–^{19}F coupling patterns, and the J_{CF} values are listed in Table IV. The ^{13}C chemical shifts and J_{CF} values of 1- and 2-fluoroadamantane have been reported earlier[32,33] and our values (which are within experimental error from those reported) are included for comparison with the ^{13}C chemical shifts of 1,3-di-, 1,3,5-tri-, and 1,3,5,7-tetrafluoroadamantanes (**3–5**).[32] However, the J_{CF} values for the polyfluoroadamantanes, **3–5**, reported in the present study are based on spin simulation technique (vide infra). No NMR parameters for the fluorodiamantanes have been reported earlier (Tables III and IV).

(a) Fluoroadamantanes. 1-Fluoroadamantane (**1**) shows the expected four carbon resonances, all of them being split into doublets due to fluorine coupling. The chemical shifts and ^{13}C–^{19}F coupling constants have been reported earlier[21,22] and require no further comments. It must, however, be pointed out that the $^{3}J_{C_3F}$ value of 9.9 Hz has been earlier suggested[22] to be not only due to the through-bond interaction but also due to the through-space 1,3-interaction of the fluorine and the C_3 (bridgehead) carbon.

2-Fluoroadamantane (**2**), characteristic of its C_s symmetry, shows seven carbon resonances, and all but C_5 ($C_{\delta_{syn}}$) are split into doublets due to fluorine coupling. The vicinal ^{13}C–^{19}F coupling constant (^{3}J) is of interest in that its magnitude is much dependent on the dihedral angle between the C_α–F and C_β–C_γ bonds. Carbons (C_8 and C_{10}) that are antiperiplanar to the C_2–F group show larger coupling constant (9.1 Hz) whereas carbons (C_4 and C_9) that are gauche to the C_2–F group have very small coupling constants (1.1 Hz). This is in support of the Karplus-type equation

Table II. ^{13}C and ^{19}F Chemical Shifts in Fluoroadamantanes

compd	^{13}C NMR chemical shifts,[a,b,c] $\delta(^{13}C)$										^{19}F NMR chemical shifts,[d] $\delta(^{19}F)$
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	
1	92.2, d (+63.8)	42.7, d (+5.0)	31.5, d (+3.1)	35.9, d (−1.8)	31.5, d (+3.1)	35.9, d (−1.8)	31.5, d (+3.1)	42.7, d (+5.0)	42.7, d (+5.0)	35.9, d (−1.8)	−129.1
3	93.1, dd (+64.7)	48.1, t (+10.4)	93.1, dd (+64.7)	41.2, m (+3.5)	31.4, t (+3.0)	34.2, t (−3.5)	31.4, t (+3.0)	41.2, m (+3.5)	41.2, m (+3.5)	41.2, m (+3.5)	−134.6
4	92.3, m (+63.9)	46.9, m (+9.2)	92.3, m (+63.9)	46.9, m (+9.2)	92.3, m (+63.9)	3.42, t (−3.5)	28.0, q (−0.4)	39.9, m (+2.2)	46.9, m (+9.2)	39.9, m (+2.2)	−141.8
5	90.0, dq (+61.6)	46.1, m (+8.4)	90.0, dq (+61.6)	46.1, m (+8.4)	90.0, dq (+61.6)	46.1, m (+8.4)	90.0, dq (+61.6)	46.1, m (+8.4)	46.1, m (+8.4)	46.1, m (+8.4)	−151.3
6	32.7, d (+4.3)	95.3, d (+57.6)	32.7, d (+4.3)	31.3, d (−6.4)	27.2, s (−1.2)	37.1, d (−0.6)	26.8, d (−1.6)	35.6, d (−2.1)	31.3, d (−6.4)	35.6, d (−2.1)	−174.9[e]
adamantane[24]	28.4	37.7	28.4	37.7	28.4	37.7	28.4	37.7	37.7	37.7	

[a] Chemicals shifts are in ppm (±0.05) with respect to external Me_4Si in $CDCl_3$ at 20 °C. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet, dd = doublet of doublets, dq = doublet of quartets—these refer to C–F coupling patterns. [c] The values in parentheses are the differences between fluoroadamantanes and the parent hydrocarbon (adamantane). [d] Chemical shifts are in ppm (±0.1) with respect to external $CFCl_3$ in $CDCl_3$ at 20 °C; negative sign indicates upfield shift. [e] $^{2}J_{HF}$ = 54.3 Hz.

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Table III. ^{13}C and ^{19}F NMR Chemical Shifts in Fluorodiamantanes

compd	^{13}C NMR chemical shifts,^{a,b,c} $\delta(^{13}C)$														^{19}F NMR chemical shifts,^{d} $\delta(^{19}F)$
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	
6	94.5, d (+56.9)	41.8, d (+4.2)	32.4, d (−5.9)	24.8, s (−1.1)	37.5, d (−0.8)	36.3, d (−1.3)	40.6, d (+3.0)	36.9, d (−1.4)	30.6, d (+4.7)	36.9, d (−1.4)	40.6, d (+3.0)	41.8, d (+4.2)	43.1, d (+4.8)	32.4, d (−5.9)	−142.5
7	36.8, d (−0.8)	40.3, d (+2.7)	42.9, d (+4.6)	92.4, d (+66.5)	42.9, d (+4.6)	40.3, d (+2.7)	36.8, d (−0.8)	36.2, d (−2.1)	25.4, d (−0.5)	36.2, d (−2.1)	36.8, d (−0.8)	40.3, d (+2.7)	36.2, d (−2.1)	42.9, d (+4.6)	−140.5
9	92.9, d (+55.3)	43.8, m (+6.2)	31.3, m (−7.0)	29.7, m (+3.8)	42.4, m (+4.1)	92.9, d (+55.3)	43.8, m (+6.2)	31.3, m (−7.0)	29.7, m (+3.8)	31.3, m (−7.0)	43.8, m (+6.2)	43.8, m (+6.2)	42.4, m (+4.1)	31.3, m (−7.0)	−150.5
9^{f}	93.2	44.8	31.0	29.5	42.3	93.2	44.8	31.0	29.5	42.3	44.8	44.8	42.3	31.0	
10	39.1, m (+1.5)	39.1, m (+1.5)	41.6, m (+3.3)	91.5, d (+65.6)	41.6, m (+3.3)	39.1, m (+1.5)	39.1, m (+1.5)	41.6, m (+3.3)	91.5, d (+65.6)	41.6, m (+3.3)	39.1, m (+1.5)	39.1, m (+1.5)	41.6, m (+3.3)	41.6, m (+3.3)	−142.1
10^{g}	39.5	39.5	40.8	91.9	40.8	39.5	39.5	40.8	91.9	40.8	39.5	39.5	40.8	40.8	
8	31.5, d (−6.1)	41.6, d (+4.0)	95.8, d (+57.5)	30.4, d (+4.5)	35.4, d (−2.9)	36.1, d (−1.5)	35.8, d (−1.8)	37.1, d (−1.2)	26.2, s (+0.3)	37.7, s (−0.6)	37.0, d (−0.6)	36.5, s (−1.1)	37.0, s (−1.3)	32.1, d (−6.2)	−179.0^{e}
diamantane	37.6	37.6	38.3	25.9	38.3	37.6	37.6	38.3	25.9	38.3	37.6	37.6	38.3	38.3	

[a] Chemical shifts are in ppm (±0.05) with respect to external Me_4Si in $CDCl_3$ at 20 °C.
[b] s = singlet, d = doublet, m = complex multiplet—these refer to ^{13}C–^{19}F coupling constants.
[c] The values in parenthesis are the differences between fluorodiamantane and the parent hydrocarbon (diamantane).
[d] Chemical shifts are in ppm (±0.1) with respect to external $CFCl_3$ in $CDCl_3$ at 20 °C; negative sign indicates upfield shift.
[e] $^2J_{HF} = 51.9$ Hz.
[f] Calculated chemical shifts (in ppm) from the SCS values in **6**.
[g] Calculated chemical shifts (in ppm) from the SCS values in **7**.

Table IV. ^{13}C–^{19}F NMR Coupling Constants in Fluoroadamantanes and Diamantanes

compd	^{13}C–^{19}F coupling constants ($^nJ_{CF}$)^a
1	$^1J_{C_1F} = -183.4$, $^2J_{C_2F} = +17.0$, $^3J_{C_3F} = 9.9$, $^4J_{C_4F} = 2.1$
2	$^1J_{C_2F} = -178.4$, $^2J_{C_1F} = +17.8$; $^3J_{C_8F} = 9.1$; $^3J_{C_4F} = 1.1$, $^4J_{C_7F} = 1.7$, $^4J_{C_5F} \simeq 0$, $^5J_{C_6F} = 0.8$
3	$^1J_{C_1F} = -187.8$, $^2J_{C_2F} = +18.8$, $^2J_{C_4F} = +18.1$,^{b} $^3J_{C_1F} = 13.3$, $^3J_{C_5F} = 10.3$, $^4J_{C_6F} = 2.1$, $^4J_{C_4F} = -2.1^b$
4	$^1J_{C_1F} = -190.7$,^{b} $^2J_{C_2F} = +19.4$,^{b} $^2J_{C_6F} = +18.7$,^{b} $^3J_{C_1F} = +14.6$,^{b} $^3J_{C_7F} = 11.4$, $^4J_{C_2F} = -1.3$,^{b} $^4J_{C_6F} = -1.3^b$
5	$^1J_{C_1F} = -191.9$, $^2J_{C_2F} = +19.9$,^{b} $^3J_{C_1F} = 17.0$, $^4J_{C_2F} = -0.7^b$
6	$^1J_{C_1F} = -186.9$, $^2J_{C_{13}F} = +18.6$, $^2J_{C_2F} = +17.6$, $^3J_{C_9F} = 10.0$, $^3J_{C_7F} = 7.7$, $^3J_{C_3F} = 1.4$, $^4J_{C_6F} = 1.5$, $^4J_{C_8F} = 2.2$, $^4J_{C_4F} \simeq 0$, $^5J_{C_5F} = 1.0$
7	$^1J_{C_4F} = -182.4$, $^2J_{C_3F} = +17.1$, $^3J_{C_2F} = 10.5$, $^4J_{C_1F} = 2.4$, $^5J_{C_8F} = 1.8$, $^6J_{C_9F} = 0.5$
8	$^1J_{C_3F} = -177.6$; $^2J_{C_4F} = +17.9$, $^2J_{C_2F} = +17.4$, $^3J_{C_5F} = 9.4$, $^3J_{C_7F} = 8.4$, $^3J_{C_{14}F} = 1.1$, $^3J_{C_1F} = 1.0$, $^4J_{C_8F} = 2.1$, $^4J_{C_6F} = 1.5$, $^4J_{C_{12}F} \simeq 0$, $^4J_{C_{13}F} \simeq 0$, $^5J_{C_{11}F} = 0.7$
9	$^1J_{C_1F} = -188.0$, $^2J_{C_2F} = +18.7$,^{b} $^2J_{C_5F} = +18.3$,^{b} $^3J_{C_4F} = +10.0$,^{b} $^3J_{C_2F} = +8.0$,^{b} $^3J_{C_3F} = +2.5$,^{b} $^4J_{C_3F} = -1.7$,^{b} $^4J_{C_4F} = -0.3$,^{b} $^4J_{C_1F} \simeq 0$, $^5J_{C_5F} = +0.4^b$
10	$^1J_{C_4F} = -183.4$, $^2J_{C_3F} = +18.4$,^{b} $^3J_{C_2F} = +11.0$,^{b} $^4J_{C_1F} = -2.2$,^{b} $^5J_{C_3F} = +2.3$,^{b} $^6J_{C_4F} \simeq 0$

[a] All coupling constants are in Hz and are accurate to ±0.25 Hz. The sign of ^1J and ^2J are assumed to be negative and positive, respectively. Signs of other coupling constants, wherever indicated, are based on their relative signs with respect to ^2J. [b] Calculated values.

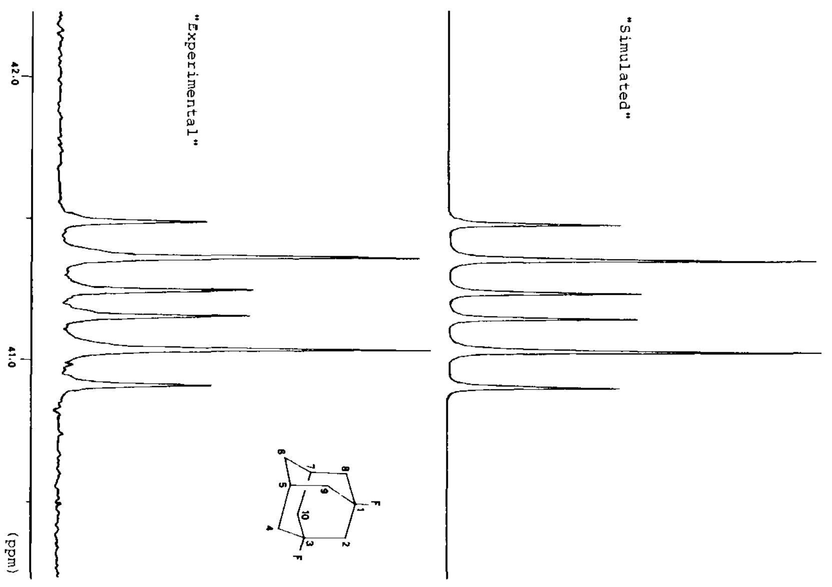

Figure 1. C_4 NMR resonance of 1,3-difluoroadamantane (**3**) in $CDCl_3$ at 20 °C.

suggested by Schneider et al.[21] It should also be noted that C_4–F ($C_{\gamma syn}$–F) coupling constant (^3J) is in fact less than the C_7–F ($C_{\delta_{anti}}$–F) coupling constant (^4J). Also, whereas C_5 ($C_{\delta_{syn}}$) has no resolvable coupling with fluorine, the remote carbon, C_6 (C_ϵ) is split into a doublet with a coupling constant of 0.8 Hz.

1,3-Difluoroadamantane, (**3**), due to its C_{2v} symmetry, shows five sets of ^{13}C resonances. Whereas, C_1, C_2, C_5, and C_6 show expected fluorine coupling patterns (C_1 being doublet of doublets and C_2, C_5, and C_6 being triplets), C_4 resonance at 41.2 ppm is a six-line pattern (as shown in Figure 1) which is characteristic of the X part of an ABX spin system.[34] This is contrary to

Table V. Calculated Values of $^{19}F-^{19}F$ Coupling Constants and ^{13}C Isotope Induced ^{19}F Chemical Shift Difference

compd	J_{FF}[a]	$\Delta\delta_{FF}(^{13}C)$[b 36]
3	+10.0	$\Delta\delta_{FF}(^{13}C_4) = -3.3$ Hz $= -0.017$ ppm
4	+8.0	$\Delta\delta_{FF}(^{13}C_1) = -3.0$ Hz $= -0.016$ ppm
		$\Delta\delta_{FF}(^{13}C_2) = -3.3$ Hz $= -0.017$ ppm
		$\Delta\delta_{FF}(^{13}C_6) = -3.3$ Hz $= -0.017$ ppm
5	+5.9	$\Delta\delta_{FF}(^{13}C_2) = -3.0$ Hz $= -0.016$ ppm
9	±2.5	$\Delta\delta_{FF}(^{13}C_2) = -1.4$ Hz $= -0.007$ ppm
		$\Delta\delta_{FF}(^{13}C_3) = -0.5$ Hz $= -0.002$ ppm
		$\Delta\delta_{FF}(^{13}C_4) = -2.0$ Hz $= -0.011$ ppm
		$\Delta\delta_{FF}(^{13}C_5) = -3.0$ Hz $= -0.016$ ppm
10	±2.8	$\Delta\delta_{FF}(^{13}C_2) = -1.3$ Hz $= -0.007$ ppm
		$\Delta\delta_{FF}(^{13}C_3) = -2.8$ Hz $= -0.015$ ppm

[a] Coupling constants are in hertz and are accurate to ±0.25 Hz. [b] The chemical shift differences ($\Delta\delta$) are given both in Hz (±0.25)(at 188.2 MHz ^{19}F resonance frequency) and in ppm.

expectations based on simple theory, wherein the fluorines would be expected to have *identical* chemical shifts and thus C_4 would be, at most, a representative of AA′X system appearing as doublet of doublets. However, it should be noted that the ^{13}C atom at C_4 in 1,3-difluoroadamantane is not equivalently located with respect to the fluorines. This means that when we observe the ^{13}C resonance of the carbon in question (C_4), there will be a differential ^{13}C isotope effect on the chemical shifts of the fluorines in these molecules.[35] This differential ^{13}C isotope effect causes the C_4 resonance to appear as the X part of an ABX spin system. The J_{CF} ($^2J_{C_4F}$ and $^1J_{C_4F}$) values along with the ^{13}C isotope (at C_4) induced F–F chemical shift difference $[\Delta\delta_{FF}(^{13}C_4)]$[36,37] and the fluorine–fluorine coupling constants ($^4J_{FF}$) can be calculated by spin simulation followed by spectral fitting with the experimental spectrum using the program LAME in the iterative mode.[38,39] Initial guesses of the coupling constants (J_{CF}) were based on the values in 1-fluoroadamantane(**1**). Values of 18 Hz for $^2J_{C_4F}$ and 2 Hz for $^4J_{C_4F}$ were assumed. Several trials were run with different values of $^4J_{FF}$ and $\Delta\delta_{FF}(^{13}C)$ and a spectral fit with the observed spectrum within ~2 Hz could be made with a $^4J_{FF}$ value of 10 Hz and a $\Delta\delta_{FF}(^{13}C_2)$ of -3 Hz. Moreover, $^2J_{C_4F}$ and $^4J_{C_4F}$ have opposite sign. Since $^2J_{CF}$ values have been earlier shown to be positive[40] $^4J_{C_4F}$ was assumed to be -2 Hz.

The chemical shifts and the coupling constants were iterated starting with these initial values by using the experimental spectrum as reference. Iterations were continued until the root-mean-square (rms) frequency error reaches a minimum. The final calculated spectrum is shown in Figure 1 along with the experimental spectrum. The final calculated values of $^2J_{C_4F}$, $^4J_{C_4F}$, $^4J_{FF}$, and $\Delta\delta_{FF}(^{13}C)$ are +18.1, -2.0, +10.0, and -3.3[36] (at 188.2-MHz ^{19}F resonance) Hz, respectively. (Note: all the above frequencies are rounded to the first decimal point.) The RMS frequency error was 0.014 Hz, indicating a very good fit to the experimental spectrum. It must, however, be pointed out that we also observed identical spectral fit with $^4J_{FF} = -10.0$ Hz. A positive value of $^4J_{FF}$ is assumed on the basis that the calculated $^4J_{FF}$ values in tri- and tetrafluoroadamantanes, **4** and **5**, (vide infra) are positive. The $\Delta\delta_{FF}(^{13}C)$ and $^4J_{FF}$ values are listed in Table V.

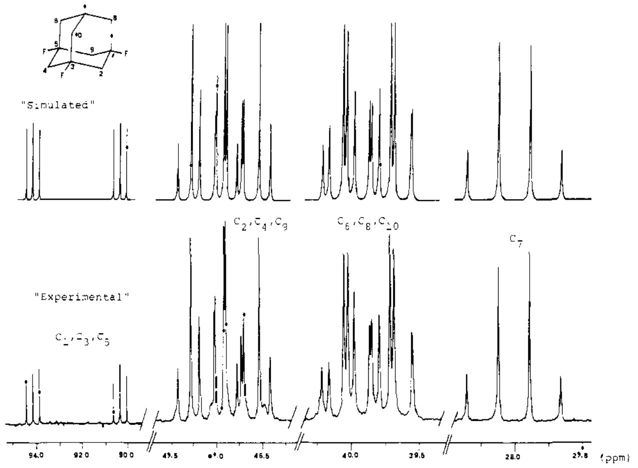

Figure 2. ^{13}C NMR spectrum of 1,3,5-trifluoroadamantane (**4**), in $CDCl_3$ at 20 °C.

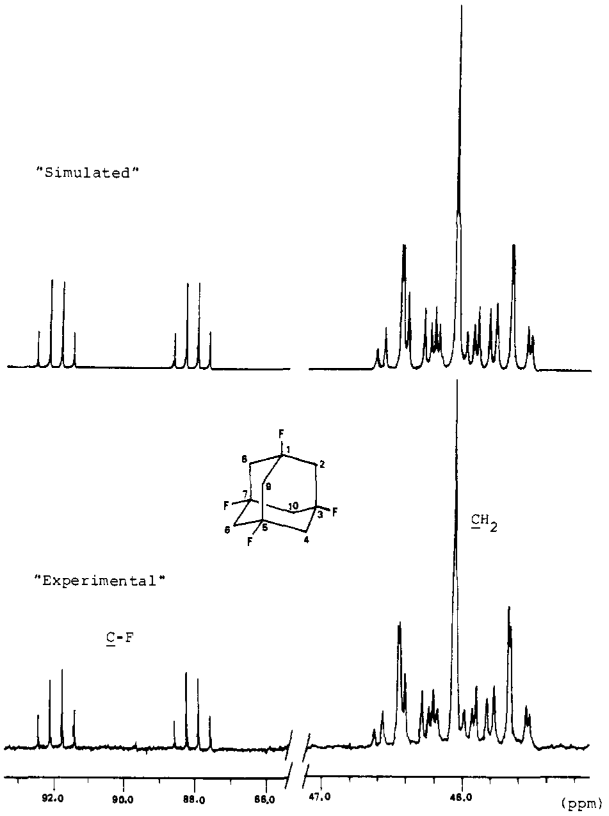

Figure 3. ^{13}C NMR spectrum of 1,3,5,7-tetrafluoroadamantane (**5**) in $CDCl_3$ at 20 °C.

One would expect a similar pattern in the ^{13}C resonance of C_1. The $^{13}C_1$ atom is also not equivalently located with respect to the fluorines thereby should introduce a differential ^{13}C isotope effect on the chemical shifts of the fluorines. However, the coupling pattern of the C_1 carbon resonance is deceptively simple (a doublet of a doublet). Indeed, given the value for the fluorine–fluorine coupling constant ($^4J_{FF}$) from the analysis of the C_4 resonance, simulation of the C_1 resonance shows a simple doublet of a doublet over a wide range of $\Delta\delta_{FF}(^{13}C_1)$.

The ^{13}C NMR spectrum (Figure 2) of 1,3,5-trifluoroadamantane (**4**) shows, as expected (due to C_{3v} symmetry), four sets of resonances. Except the ^{13}C resonance of C_7, which is symmetrically located with respect to the three fluorine atoms and thus appearing as a simple quartet, all other resonances are complex multiplets. All these carbons resonances (those of C_1,

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(34) Roberts, J. D. "An Introduction to the Analysis of Spin–Spin Splitting in Nuclear Magnetic Resonance"; W. A. Benjamin: New York, 1962; pp 71–85.

(35) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2361.

(36) $\Delta\delta_{FF}(^{13}C)$ is defined as δ_F(nearer to ^{13}C) – δ_F(farther from ^{13}C) and are in general negative, as ^{13}C isotope shields a fluorine compare to ^{12}C isotope.[37]

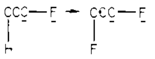
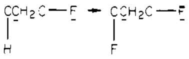
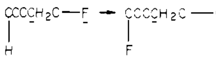
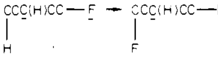
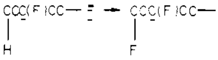
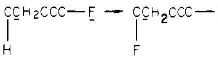
(37) Batiz-Hernandez, H.; Bernheim, R. A. "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsley, J. W., Feeney, V. Sutcliff, L. M., Eds.; Pargamon Press: New York, 1967; Vol. 3, Chapter 2.

(38) The spin simulation is based on the Fortran program LAME, which is LAOCOON with magnetic equivalence added.[39] LAME calculates the theoretical spectrum for spin-$^1/_2$ nuclei given the values of chemical shifts and coupling constants. It can adjust the values of the parameters to approach a given experimental spectrum.

(39) (a) Bothner-by, A. A.; Castellano, S. *J. Chem. Phys.* **1964**, *41*, 3863. (b) Emsley, J. W., Feeney, V., Sutcliffe, L. M., Eds., "Progress in Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1966; Vol. 1, Chapter 3. (c) Stanley, R. M.; Marquardt, D. W.; Ferguson, R. C. *J. Chem. Phys.* **1964**, *41*, 2087.

(40) (a) Tiers, A. V. D.; Lauterber, P. C. *J. Chem. Phys.* **1962**, *36*, 1110. (b) Bernheim, R. A.; Lavery, B. J. *J. Am. Chem. Soc.* **1967**, *89*, 1279.

Table VI. Comparison of ^{13}C–^{19}F Coupling Constants in Fluoroadamantanes[a]

$^{n}J_{CF}$	coupling constants, Hz	comments
$^{1}J_{CF}$	$^{4}J_{C_1F}$(**1**), −183.4 > $^{1}J_{C_1F}$(**3**), −187.8 > $^{1}J_{C_1F}$(**4**), −190.7 > $^{1}J_{C_1F}$(**5**), −191.9	 $\underset{\underset{H}{\vert}}{C}C\underline{C}—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}C\underline{C}—\underline{F}$
$^{2}J_{CF}$	$^{2}J_{C_2F}$(**1**), 17.0 < $^{2}J_{C_2F}$(**3**), 18.8 $^{2}J_{C_4F}$(**3**), 18.1 < $^{2}J_{C_2F}$(**4**), 19.4 $^{2}J_{C_6F}$(**4**), 18.7 < $^{2}J_{C_2F}$(**5**), 19.9	 $\underset{\underset{H}{\vert}}{C}\underline{C}H_2C—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}\underline{C}H_2C—\underline{F}$
	$^{2}J_{C_2F}$(**1**), 17.0 < $^{2}J_{C_4F}$(**3**), 18.1 < $^{2}J_{C_6F}$(**4**), 18.7	 $\underset{\underset{H}{\vert}}{C}CC\underline{C}H_2C—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}CC\underline{C}H_2C—\underline{F}$
$^{3}J_{CF}$	$^{3}J_{C_3F}$(**1**), 9.9 < $^{3}J_{C_3F}$(**3**), 13.3 $^{3}J_{C_5F}$(**3**), 10.3 < $^{3}J_{C_5F}$(**4**), 14.6 $^{3}J_{C_7F}$(**4**), 11.4 < $^{3}J_{C_1F}$(**5**), 17.0	$H—\underline{C}CC—\underline{F} \rightarrow F—\underline{C}CC—\underline{F}$
	$^{3}J_{C_3F}$(**1**), 9.9 < $^{3}J_{C_5F}$(**3**), 10.3 < $^{3}J_{C_7F}$(**4**), 11.4	 $\underset{\underset{H}{\vert}}{C}C\underline{C}(H)CC—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}C\underline{C}(H)CC—\underline{F}$
	$^{3}J_{C_3F}$(**3**), 13.3 < $^{3}J_{C_3F}$(**4**), 14.6 < $^{3}J_{C_1F}$(**5**), 17.0	 $\underset{\underset{H}{\vert}}{C}C\underline{C}(F)CC—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}C\underline{C}(F)CC—\underline{F}$
$^{4}J_{CF}$	$^{4}J_{C_4F}$(**1**), −2.1 ≃ $^{4}J_{C_4F}$(**3**), −2.0 < $^{4}J_{C_2F}$(**4**), −1.3 $^{4}J_{C_6F}$(**4**), −1.3 < $^{4}J_{C_2F}$(**5**), −0.7	 $\underset{\underset{H}{\vert}}{C}\underline{C}H_2CCC—\underline{F} \rightarrow \underset{\underset{F}{\vert}}{C}\underline{C}H_2CCC—\underline{F}$
	$^{4}J_{C_4F}$(**1**), −2.1 = $^{4}J_{C_6F}$(**3**), −2.1 $^{4}J_{C_4F}$(**3**), −2.0 < $^{4}J_{C_6F}$(**4**), −1.3 $^{4}J_{C_2F}$(**4**), −1.3 < $^{4}J_{C_2F}$(**5**), −0.7	$H—CCC\underline{C}H_2CCC—\underline{F} \rightarrow F—CCC\underline{C}H_2CCC—\underline{F}$

[a] Comparisons shown here are those between compounds that differ in their structure as depicted in the comments.

C_2, and C_6) appear as the X part of an A2BX (or AB2X) spin system for the same reason as discussed earlier for the C_4 resonance of **3**. Each multiplet was analyzed independently as X part of A2BX spin system using the program LAME in the interative mode. The calculated values of $^{n}J_{CF}$ are given in Table III. The $^{4}J_{FF}$ value of +8.0 Hz was obtained in all the three analyses. The rms frequency errors at the end of the iterations are <0.1 Hz, indicating good fit with the experimental spectrum. The calculated spectrum is shown in Figure 2 along with the experimental spectrum. The $^{4}J_{FF}$ and $\Delta\delta_{FF}(^{13}C)$[36] values are given in Table V.

1,3,5,7-Tetrafluoroadamantane (**5**) having the same (T_d) symmetry as adamantane shows two ^{13}C resonances at $\delta_{^{13}C}$ 90.0 and 46.1. As shown in Figure 3, the C_2 resonance at 46.1 ppm is a complex pattern representative of the X part of A2B2X spin system. The multiplet was analyzed again by spin simulation and spectral fitting (rms frequency error, 0.04 Hz). The calculated values of $^{4}J_{FF}$ and $\Delta\delta_{FF}(^{13}C)$ are given in Table V and those of $^{2}J_{CF}$ and $^{4}J_{CF}$ are listed in Table IV. The calculated spectrum is also shown in Figure 3. Again, the C_1 resonance, although expected to be X part of AB3X spin system, is deceptively simple (doublet of quartets). Spin simulation does indeed show a simple pattern (Figure 3).

The differences in chemical shifts ($\Delta\delta_{^{13}C}$) between the fluoroadamantanes and the parent hydrocarbon, adamantane, are listed in Table II. A nonadditivity of SCS (substituent effects on ^{13}C chemical shifts) values is observed. Such deviations of observed SCS values from additivity in 2-substituted adamantanes,[41] 4-substituted adamantanones,[41,42] and 2,4-disubstituted adamantanes[43] have been discussed earlier in terms of different interaction mechanisms operating through the σ-bond framework or through space. Analysis of these data, however, reveal some interesting patterns of SCS (substitutent effects on ^{13}C chemical shifts) values. The β SCS values range between 5.0 and 6.2 ppm and increase in the following order: adamantane → **1** ($\Delta\delta_{C_2}$ = 5.0 ppm) < **1** → **3** ($\Delta\delta_{C_2}$ = 5.4 and $\Delta\delta_{C_4}$ = 5.3 ppm) < **3** → **4** ($\Delta\delta_{C_4}$ = $\Delta\delta_{C_6}$ = 5.7 ppm) < **4** → **5** ($\Delta\delta_{C_6}$ = 6.2 ppm). The β SCS value is shown to increase by ~0.4 ppm progressively for the introduction of every additional fluorine atom into the adamantane skeleton. The δ SCS value also shows the same trend. This value, however, is negative and increases in the order: adamantane → **1** ($\Delta\delta_{C_4}$ = −1.8 ppm) < **1** → **3** ($\Delta\delta_{C_6}$ = 1.7 and $\Delta\delta_{C_8}$ = −1.5 ppm) < **3** → **4** ($\Delta\delta_{C_2}$ = −1.2 and $\Delta\delta_{C_8}$ = −1.3 ppm) < **4** → **5** ($\Delta\delta_{C_2}$ = −0.8 ppm). The δ SCS value, thus, increases progressively by ~0.25 ppm for every additional fluorine atom introduced into adamantane.

The α and γ SCS values, however, do not show a specific trend. The α SCS have the following values: adamantane → **1** ($\Delta\delta_{C_1}$ = 63.8 ppm), **1** → **3** ($\Delta\delta_{C_3}$ = 61.6 ppm), **3** → **4** ($\Delta\delta_{C_5}$ = 60.9 ppm), and **4** → **5** ($\Delta\delta_{C_7}$ = 62.0 ppm). The γ SCS have the following values: adamantane → **1** ($\Delta\delta_{C_3}$ = +3.1), **1** → **3** ($\Delta\delta_{C_1}$ = +1.1 and $\Delta\delta_{C_5}$ = −0.1 ppm), **3** → **4** ($\Delta\delta_{C_1}$ = −0.8 and $\Delta\delta_{C_7}$ = 3.4 ppm), and **4** → **5** ($\Delta\delta_{C_1}$ = −2.3 ppm). Thus, while we observe a definite trend in the β and δ SCS values (i.e., substituent effects on methylene carbon resonances), there is a lack of any specific trend in the α and γ SCS values (i.e., substituent effect on bridgehead-carbon resonances). This could be because, in addition to inductive and polarization factors, spacial interaction of 1,3-carbon atoms in adamantanes play a major role in shielding or deshielding of the bridgehead carbon atoms.[44]

A comparative analysis of the ^{13}C–^{19}F coupling constants in fluoroadamantanes has been made in Table VI. Specific trends in the $^{n}J_{CF}$ values can be seen in this comparison. The $^{1}J_{CF}$ values, which are negative,[40b] progressively decreases on introduction of a fluorine at the γ_{anti} carbon atom. However, $^{2}J_{CF}$ (positive), $^{3}J_{CF}$ (positive in view of the fact that it has the same sign as $^{2}J_{CF}$ in the analysis of C_2 resonance in **9** and has opposite sign with respect to $^{4}J_{CF}$ in the analysis of C_1 resonance in **10**, vide infra), and $^{4}J_{CF}$ (negative) increase progressively on introduction of a fluorine at the γ_{anti} carbon atom. It must be noted that such changes in the coupling constants with the introduction of additional fluorine atom to the system are not additive. It has been shown recently[45] that one-bond carbon–fluorine coupling constants, $^{1}J_{CF}$, in a series of fluorinated adamantane derivatives can be correlated with the Δδ values (SCS values) of the carbon atom involved in the coupling. Since the nonadditivity observed in SCS values has been earlier rationalized[41-43] on the basis of a intramolecular interaction operating through the σ-bond framework or through space, the observed correlation between $^{1}J_{CF}$ and the Δδ values have been interpreted as evidence for the sensitivity of $^{1}J_{CF}$ toward such intramolecular interactions. In the present study, we also observed nonadditivity both in the chemical shift and coupling constant values. However, the number of examples in the present study are too limited to safely draw any correlation between them.

Other interesting parameters in the present study are the calculated values of $^{4}J_{FF}$ and $\Delta\delta_{FF}(^{13}C)$ (cf. Table V). The ^{13}C isotope induced chemical shift difference in fluorine resonances [$\Delta\delta_{FF}(^{13}C)$] is in the order of −0.016 ppm and remains roughly the same in all the polyfluoroadamantanes. The $^{4}J_{FF}$ coupling

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(41) Duddeck, H. *Org. Magn. Son.* **1975**, *7*, 151.

(42) Duddeck, H.; Wolff, P. *Org. Magn. Reson.* **1977**, *9*, 528.

(43) (a) Duddeck, H. *Tetrahedron* **1978**, *34*, 247. (b) Duddeck, H.; Feuerheln. *Tetrahedron* **1980**, *36*, 3009.

(44) Adcock, W.; Dewar, M. J. S.; Golden, R.; Zeb, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 2198.

(45) Duddeck, H.; Islam, Md. R. *Tetrahedron* **1981**, *37*, 1193.

constant, on the other hand, is positive and decreases in the order difluoro- >trifluoro-> tetrafluoroadamantane. Introduction of every additional fluorine atom decreases the coupling constant ($^4J_{FF}$) by ~2 Hz.

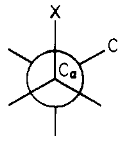
(b) Fluorodiamantanes. Diamantane, the next higher adamantalogue of adamantane has two kinds of bridgehead positions (belt, i.e., C_1, C_2, C_6, C_7, C_{11}, and C_{12}, and apical, i.e., C_4 and C_9). Both bridgehead-substituted monofluorodiamantanes (**6** and **7**), the secondary 3-fluorodiamantane (**8**), and two symmetrical difluorodiamantanes (1,6- and 4,9-fluorodiamantanes (**9** and **10**, respectively)) were prepared and studied in the present investigation.

The monofluorodiamantanes, **6**, **7**, and **8**, show 10, 6, and 14 ^{13}C resonances, respectively, characteristic of their C_s, C_{3v}, and C_1 symmetry. The chemical shifts and the $^nJ_{CF}$ values are tabulated in Tables III and IV.

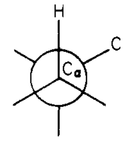
1,6-Difluorodiamantanes (**9**) shows five ^{13}C resonances as would be expected from its D_{2h} symmetry. Except for the C_1 resonance all the ^{13}C resonances have six-line patterns(^{13}C–^{19}F coupling patterns) characteristic of the X part of the ABX spin system, similar to that observed for the C_4 resonance in 1,3-difluoroadamantane (**3**). The $^nJ_{CF}$ values were calculated as described earlier and are listed in Table IV. The $^5J_{FF}$ and $\Delta\delta_{FF}(^{13}C)$ values were also calculated from each of the ^{13}C multiplets and are listed in Table V along with those in polyfluoroadamantanes. The rms frequency error with respect to the experimental spectrum in these calculations is in the order 0.01–0.06 Hz, indicating a very good spectral fit.

4,9-Difluorodiamantane (**10**) has the same symmetry as diamantane itself (D_{3d}) and shows three carbon resonances. Again, except for the C_4 resonance, the other two resonances have six-line patterns (ABX spin system) and were analyzed as before. The $^nJ_{CF}$ values are listed in Table IV and the calculated $\Delta\delta_{FF}(^{13}C)$ values are listed in Table V along with $^7J_{FF}$ value. The rms frequency error in this case is 0.02–0.04 Hz.

The α-SCS for fluorine in the diamantane skeleton is 56.9 and 66.5 ppm, respectively, for 1-fluoro- and 4-fluorodiamantanes (**6** and **7**). It has been pointed out[26,46] that for bridgehead-substituted compounds the large differences of α-SCS are mainly caused by the varying number of the gauche interactions (XC) between the substituent X and the γ carbon atoms



[XC]

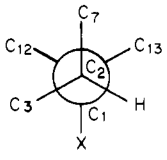


[HC]

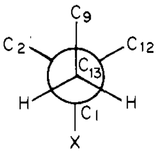
The gauche interaction XC replaces the interaction HC so that the net contribution from the X–C interaction is [XC – HC].[46]

In 4-fluorodiamantane no [XC – HC] interaction is present, whereas in 1-fluorodiamantane two gauche interactions exist. From these α-SCS values [FC – HC] contribution can be estimated to b ~–4.8 ppm. It must be noted that the α-SCS value in 1-fluoroadamantane (63.8 ppm) is close to that in 4-fluorodiamantane (66.5 ppm), both the compounds having no [XC – HC] gauche interaction.

The β-SCS values in **6** are 4.2 (for C_2) and 4.8 ppm (for C_{13}) and in **7** is 4.6 (for C_3) ppm. The difference between the two β-SCS values in **6** can again be explained by the differences in the number of gauche interactions.



CX + HX



2HX

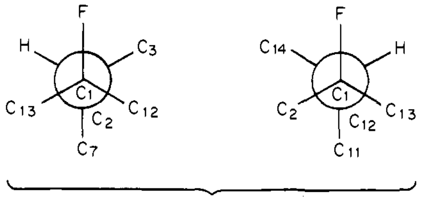
Since the numerical values of the CX and HX gauche interactions are different and HX > CX,[39] the β-SCS values become larger with increasing number of HX interactions (as in C_{13}).

The γ_{syn} and γ_{anti} effects have been studied earlier by several groups[26,47] and require no further comments. The γ_{syn} and γ_{anti} carbons as expected are shielded and deshielded, respectively, in both **6** and **7**. The δ, ϵ, and the other remote carbons are slightly shielded in **6** and **7** with respect to diamantane.

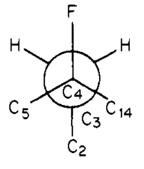
The carbon chemical shifts in difluorodiamantanes (**9** and **10**) have also been calculated using the SCS values obtained from **6** and **7**, respectively, and are given in Table III for comparison with the experimental values. The experimental chemical shift values are within ±1 ppm from the calculated ones indicating that the SCS is additive in these cases. However, it would be erroneous to extrapolate this additivity to tri- and tetrafluorodiamantanes,[48] in view of the fact that the SCS values in fluoroadamantanes progressively change on introduction of each additional fluorine atom in the molecule (vide supra).

The $^1J_{C_4F}$, $^2J_{C_3F}$, $^3J_{C_2F}$, and $^4J_{C_1F}$ values in **7** compare well with the corresponding values ($^1J_{C_1F}$, $^2J_{C_2F}$, $^3J_{C_3F}$, and $^4J_{C_1F}$, respectively) in 1-fluoroadamantane. It is interesting to note that C_8 and even C_9 have resolvable coupling with the fluorine (1.8 and 0.5 Hz, respectively). Transmission, in this case, of the coupling through six carbons (to C_9) could be due to the perfect antiperiplanar arrangement of all the carbon–carbon bonds involved.

Analysis of the J_{CF} values in **6** is more informative in that the fluorine atom is "axial" to one of the cyclohexane rings. The various ^{13}C–^{19}F coupling constants in **6** follow the same pattern as the SCS values. The $^1J_{CF}$ in **6** is less than the $^1J_{CF}$ value in **7** or **1** (assuming the sign of the one-bond ^{13}C–^{19}F coupling constant is negative[1]) and so is the α-SCS value. As in the case of α-SCS value, this lower value of $^1J_{CF}$ in **6** could be due to the presence of two C–F gauche interaction in **6** compared to none in **7**.



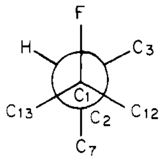
6

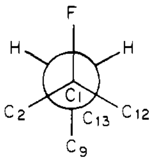


7

The magnitude of $^2J_{C_2F}$ is less than $^2J_{C_{13}F}$ (17.6 and 18.6, respectively) so is the C_2-β-SCS when compared to C_{13}-β-SCS value.

The $^3J_{C_3F}$ ($^3J_{C_{\gamma(syn)}F}$) is very small (1.4 Hz) compared to $^3J_{C_9}F$ ($^3J_{C_{\gamma(anti)}F}$, 10 Hz) or $^3J_{C_7F}$ ($^3J_{C_{\gamma(anti)}F}$, 7.7 Hz). This is in support of the Karplus-type equation suggested by Schneider et al.[21] for the vicinal ^{13}C–^{19}F coupling constant. The C_7 and C_9 carbons being antiperiplanar (dihedral angle 180°) to the C–F bond show larger coupling constant thanC_3, which is synperiplanar (dihedral angle 60°) to the C–F bond.





The observation that $^3J_{C_7F}$ is less than $^3J_{C_9F}$ (both being $^3J_{C_{\gamma(anti)}F}$) could probably be due to the presence of a CF and a HF gauche interaction in the former case compared to two HF gauche in-

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[46] Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1975**, *53*, 1307; **1976**, *54*, 632.

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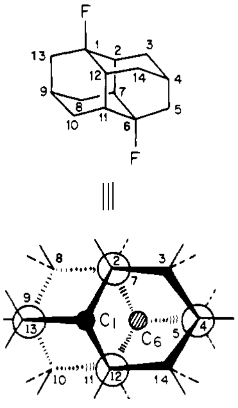
[48] Olah, G. A.; Shih, J. G.; Krishamurthy, V. V.; Singh, B. P., unpublished results.

teraction in the latter. The value of $^3J_{C_2F}$ in **7** is very close to that of $^3J_{C_9F}$ (its stereochemical counterpart) in **6**. The $^4J_{C_8F}$ values in both **6** and **7** are in the order of 1.5–2.5 Hz while the $^5J_{C_xF}$ in **6** ($^5J_{C_5F}$) is 1.0 Hz and that in **7** ($^5J_{C_8F}$) is 1.8 Hz.

The coupling constants in the difluorodiamantanes, **9** and **10**, follow the same pattern as in the corresponding monofluorodiamantanes, **6** and **7**, respectively. Particularly, it must be pointed out that the vicinal couplings (^3J) are as predicted from the Karplus-type relationship with the dihedral angle and the number of CF gauche interactions.

The ^{13}C isotope induced fluorine chemical shift differences [$\Delta\delta_{FF}(^{13}C)$] and the J_{FF} coupling constants in **9** and **10** are listed in Table V. The $\Delta\delta_{FF}(^{13}C)$ values in **9** are in the following order: $\Delta\delta_{FF}(^{13}C_5)$ (–0.016 ppm) > $\Delta\delta_{FF}(^{13}C_4)$ (–0.011 ppm) > $\Delta\delta_{FF}(^{13}C_2)$ (–0.007 ppm) > $\Delta\delta_{FF}(^{13}C_3)$ –0.002 ppm). The C_5 carbon (β to one and ϵ to the other fluorine) shows higher differential ^{13}C isotope effect followed by C_4 (γ_{anti} to one and δ to the other fluorine), C_2 (β to one and γ_{anti} to the other), and C_3 (γ_{syn} to one and δ to the other). This is in line with the expectation that the carbon that is most unsymmetrically placed (i.e., C_5) with respect to the fluorines should induce maximum ^{13}C isotope induced fluorine chemical shift difference [$\Delta\delta_{FF}(^{13}C)$] compared to the one that is more symmetrically placed (i.e., C_2). It must also be noted that C_4, which is γ_{anti} to one and δ to the other fluorine, induces more chemical shift difference in fluorine than C_3, which is γ_{syn} to one and δ to the other. Analysis of the $\Delta\delta_{FF}$ values in **10** also reveal the same pattern. A ^{13}C isotope at C_2, which is γ to one and δ to another fluorine, induces less chemical shift difference (–0.007 ppm) than a ^{13}C isotope at C_3 (–0.015 ppm), which is β to one and ϵ to the other fluorine.

Of further interest are the ^{19}F–^{19}F coupling constants in **9** and **10**. Interestingly the $^7J_{FF}$ in **10** (±2.8 Hz)[49] is very close to $^5J_{FF}$ in **9** (±2.5 Hz)[49] and they are within experimental error. It may be argued that the observation that the seven-bond coupling in **10** is the same as the five-bond coupling in **9** is due a through-space interaction between the back-lobes of the C–F bonds in **10**. As can be seen from the projection formulas of **9** and **10**, the C–F bonds in **10** are coaxial with each other while in **9** they are parallel. This might be the reason for the unusually high $^7J_{FF}$ value observed in **10**, which is in fact even slightly higher (~0.3 Hz) than the $^5J_{FF}$ value in **9**.



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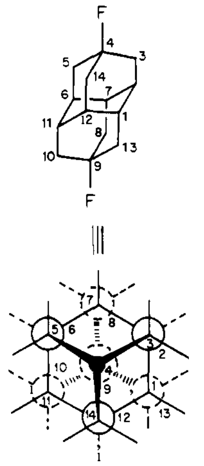

10

3-Fluorodiamantane (**8**) was also prepared for the present study from 3-diamantanol, and its ^{13}C and ^{19}F NMR data are listed in Tables III and IV. The Analysis of the SCS and $^nJ_{CF}$ values in **8** is straightforward. They have the expected pattern from the analysis of **2** and **6**.

Conclusion

In summary specific trends in SCS values and $^nJ_{CF}$ coupling constants were observed in a series of fluoroadamantanes. Although the changes in the SCS or $^nJ_{CF}$ values on introduction of each additional fluorine atom into adamantane skeleton are not additive, they follow a specific pattern. Study of mono- and difluorodiamantane shows that the SCS and $^nJ_{CF}$ values can be analyzed in terms of the number and type of gauche interaction present in the system. The unique "stereoposition" of the C_4 and C_9 carbon atoms in diamantane is proposed as the reason for the unusually large seven-bond fluorine–fluorine coupling in 4,9-difluorodiamantanes. Study of tri- and tetrafluorodiamantanes is expected to provide further useful information in this regard, and our work is being continued toward this.[48]

Experimental Section

All the bridgehead adamantanoid fluorides, except **7**, were prepared from the corresponding bromides or chlorides using $PPHF/NO_2^+BF_4^-$[29] as described in the following general procedure. The secondary fluorides **2** and **8** and the bridgehead fluoride **7** were prepared from the corresponding alcohols by using HF/Py.[28] The halo compounds were prepared from adamantane or diamantane by using literature procedures.[30,31] All compounds were analyzed by ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts of all adamantyl fluorides compare satisfactorily with the literature data.[32] The diamantyl fluorides gave satisfactory elemental analyses (Table I).

The ^{13}C NMR spectra were recorded in $CDCl_3$ (which also acts as deuterium source for internal field-frequency lock) solution (~10% w/v) at room temperature in Varian XL-200 superconducting NMR spectrometer at 50.3-MHz ^{13}C operating frequency with broad-band proton noise decoupling. Spectra were typically recorded with 4-KHz spectral width and 4-s acquisition time. Data acquisition was continued with a repitition rate of 6 s until satisfactory S/N was obtained. The FID's were Fourier transformed with 32 K Fourier number. The digital resolution under these conditions is 0.25 Hz. Chemical shifts are referenced to external Me_4Si and the assignments are on the basis of their position, carbon–fluorine coupling pattern and magnitude, and proton multiplicities obtained by using APT (attached proton test)[51] experiments.

All ^{19}F spectra were recorded in $CDCl_3$ solution (~10% w/v) at room temperature in a Varian XL-200 NMR spectrometer at 188.2-MHz ^{19}F operating frequency. The chemical shifts are referenced to external $CFCl_3$ and are accurate to ±0.1 ppm.

Spin simulation and spectral fitting are based on standard Fortran program, LAME.[38,39] Initial guesses of $^nJ_{CF}$ were made by using the corresponding values in monofluoro compounds. The values of $^nJ_{CF}$, J_{FF}, and $\Delta\delta_{FF}(^{13}C)$ were adjusted by trial to approach the experimental spectrum within 1–2 Hz. The coupling constants and the chemical shifts are then iterated to approach the given experimental spectrum. The iterations were continued util the root-mean-square (rms) frequency error reaches a minimum. In general, rms frequency errors at the end of the iterations are <0.1 Hz with respect to the given experimental spectrum. The relative sign of the coupling constants are based on the initial assumption that $^2J_{CF}$ is positive.[40] Wherever $^2J_{CF}$ is not involved in the calculation $^4J_{CF}$ is assumed to be negative.[50] The fluorine nearer to a ^{13}C isotope is always assumed to be shielded compared to the one farther from ^{13}C.[37] In other words, $\Delta\delta_{FF}(^{13}C)$[36] was always assumed to be negative.

General Procedure for the Preparation of Bridgehead Fluorides from the Corresponding Bromides. The reaction time, temperature, reactant ratio, and yields are listed in Table I.

To a solution of $NO_2^+BF_4^-$ in 30–35 mL of pyridine polyhydrogen fluoride[28] (70%) in a 100-mL pressure reaction vessel (Teflon bottle can be used for reactions at room temperature) at 0 °C the corresponding bridgehead halide in 10–15 mL of dry CH_2Cl_2 was added with continuous stirring. After the addition the reaction mixture was stirred at appropriate temperature for the required time (cf. Table I). The mixture was poured into crushed ice and extracted with (2 × 100 mL) ether. The organic layer was washed successively with water, saturated $NaHCO_3$ solution, and finally with brine and dried over $MgSO_4$ and the solvent distilled at low pressure. The fluoride obtained was >90% pure and was further purified by chromatography on silica gel column with hexane–

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(49) The relative sign of $^5J_{FF}$ in **9** and $^7J_{FF}$ in **10** with respect to J_{CF} could not be determined. Spectral fitting with positive or negative J_{FF} gave identical results.

(50) This assumption is based on the results of the present study: whenever $^2J_{CF}$ and $^4J_{CF}$ were involved in the calculation, they have opposite signs.

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chloroform as eluant. Analytical samples were prepared by further recrystallization in methanol/chloroform (1:2). The purified product was analyzed by ^{13}C NMR spectroscopy. All new compounds gave satisfactory elemental analysis (cf. Table I).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. 1, 768-92-3; **1** bromide, 768-90-1; **2**, 16668-83-0; **2** alcohol, 700-57-2; **3**, 54043-61-7; **3** chloride, 16104-50-0; **4**, 54043-62-8; **4** bromide, 707-34-6; **5**, 54043-63-9; **5** bromide, 7314-86-5; **6**, 77052-09-6; **6** bromide, 30545-17-6; **7**, 77052-10-9; **7** alcohol, 30651-03-7; **8**, 90481-59-7; **8** alcohol, 30545-24-5; **9**, 90481-60-0; **9** bromide, 32401-10-8; **10**, 90481-61-1; **10** chloride, 32401-20-0; $NO_2^+BF^-$, 13826-86-3; PPHF, 62778-11-4.

Synthesis, Structural Characterization, and Electronic Structures of the "Mixed" Terminal Ligand Cubanes $[Fe_4S_4Cl_2(XC_6H_5)_2]^{2-}$ (X = S, O) and $[Fe_4S_4(SC_6H_5)_2(OC_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$. The First Examples of $[Fe_4S_4]^{2+}$ Cores with a Noncompressed D_{2d} Idealized Geometry

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Abstract: Mixed terminal ligand iron–sulfur clusters of the type $(Ph_4P)_2[Fe_4S_4(L)_2(L')_2]$ (L = SPh, L′ = Cl, OPh, Br; L = OPh, L′ = Cl) have been synthesized in good yields by the reaction of $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br) with 2 equiv of KSPh or NaOPh and by the reaction of $[Fe_4S_4(SPh)_2Cl_2]^{2-}$ with 2 equiv of NaOPh, respectively. The crystal structures of $(Ph_4P)_2[Fe_4S_4(XPh)_2Cl_2]$ (I, X = S; II, X = O) and $(Ph_4P)_2[Fe_4S_4(SPh)_2(OPh\text{-}p\text{-}CH_3)_2]$ (III) are described in detail. Crystalline salts of I and II show symmetry consistent with the orthorhombic space group *Pbcn* with cell $a = 13.082$ (1) Å, $b = 21.182$ (4) Å, and $c = 21.376$ (4) Å and $a = 13.060$ (3) Å, $b = 20.891$ (5) Å, and $c = 21.423$ (7) Å, respectively. Salt III belongs to the noncentrosymmetric orthorhombic space group $P2_12_12$ with cell constants $a = 24.595$ (7) Å, $b = 12.588$ (3) Å, and $c = 10.877$ (3) Å. In all structures all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the structure factor calculation but not refined. Refinement by full-matrix least squares of 334 parameters on 2203 data for I, 334 parameters on 2149 data for II, and 397 parameters on 3231 data for III gave final *R* values of 0.061, 0.061, and 0.066, respectively. The anions in I and II are located on the crystallographically imposed twofold axis. The mean Fe–S* bond lengths in I and II are 2.278 (5) and 2.285 (5) Å, respectively. The Fe_4S_4* cores in I and II represent the first examples of such cores without an overall compressed D_{2d} geometry. The anion in III also is located on a crystallographic twofold axis. The Fe_4S_4* unit can be described as slightly compressed along an axis that is perpendicular to the crystallographic twofold. The terminal Fe–SPh bond lengths in I and III are 2.261 (3) and 2.289 (3) Å, respectively. The Fe–OAr bond lengths in II and III are found at 2.057 (9) and 1.996 (9) Å, respectively. The electronic and ^1H NMR spectra and solution magnetic studies are reported. Zero field Mössbauer spectra of I, II, and III show one doublet that consists of two poorly resolved quadrupole doublets with very similar isomer shift values. A fitting procedure using two Lorentzian lines with the restriction of equal areas yields (at 77 K) $\delta_1 = 0.46$, $\Delta E_{Q1} = 0.64$, $\delta_2 = 0.48$, and $\Delta E_{Q2} = 0.96$ mm/s for I, $\delta_1 = 0.49$, $\Delta E_{Q1} = 0.78$, $\delta_2 = 0.50$, and $\Delta E_{Q2} = 1.09$ mm/s for II, and $\delta_1 = 0.48$, $\Delta E_{Q1} = 0.91$, $\delta_2 = 0.47$, and $\Delta E_{Q2} = 1.19$ mm/s for III. Cyclic voltammetric studies in CH_3CN and DMF show that I and III reduce reversibly by one electron while II shows quasi-reversible reduction.

Introduction

The redox-active, non-heme iron proteins (NHIP) ubiquitous in virtually all forms of life[2] contain inorganic Fe–S centers in a variety of structures. Crystallographic studies on numerous NHIP, from various sources,[3] have established this diversity in structure of such Fe–S centers as $Fe^{II}S_4$,[3] $Fe^{III}S_4$,[3] Fe_4S_4,[3,4] Fe_2S_2,[5] and Fe_3S_3.[6]

The synthesis of inorganic, active-site analogue complexes has been of paramount importance in understanding the fine electronic and structural details of these centers, which in a biological environment are anchored to the protein backbone via deprotonated cysteinyl residues. Detailed descriptions of the electronic and structural characteristics of such synthetic analogues as the $[Fe_4S_4(SR)_4]^{2-}$,[7–9] $[Fe_4S_4(SR)_4]^{3-}$,[10] $[Fe_2S_2(SR)_4]^{2-}$,[11] $[Fe(SR)_4]^{2-}$,[12] $[Fe(SR_4)]^-$,[13] and $[Fe(o\text{-xylyldithiol})_2]^{-,2-}$[14] complexes are now available primarily due to elegant studies by Holm, Ibers, and co-workers.[15] Comparative studies of the electronic and

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