

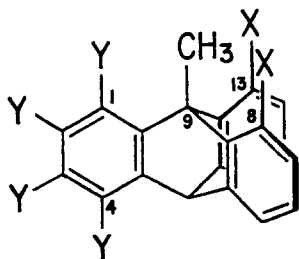
OBSERVATION OF THROUGH-SPACE SPIN COUPLINGS OF
THE INDIVIDUAL PROTONS IN A METHYL GROUP TO A ^{19}F NUCLEUS

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Summary: ^1H NMR spectrum of 8,13-dichloro-1,2,3,4-tetrafluoro-9-methyltriptycene at low temperature, where internal rotation of the methyl group is frozen, shows that 1-F couples to the *ap* proton of the methyl group with a coupling constant of 8.7 Hz and to the *sc* protons with 6.1 Hz.

Long range spin couplings between proton(s) and nearby ^{19}F nuclei by a through-space mechanism are well documented.^{1,2)} Importance of proximity and bond orientation of the coupling nuclei has been claimed.³⁾ As for the H-F coupling exhibited by a methyl group, averaged behavior of three protons in a methyl group has always been observed because of fast internal rotation of the group on the NMR time scale, and thus experimental verification of the proximity and bond orientation effects of each proton has been lacking. Our successful observation of restricted rotation of a methyl group at the bridgehead in suitably substituted triptycene derivatives⁴⁾ made us expect that 9-methyltriptycenes carrying a fluorine atom at a *peri*-position would be a good model system for such investigations. As 1,2,3,4-tetrafluoro-9-methyltriptycene (1)²⁾ showed no indication of restricted rotation of the methyl group even at -80°C , we were forced to introduce further substituents at *peri*-positions in order to raise the rotational barrier of the methyl group. In this letter, we report the first observation of H-F couplings by the three individual protons of a methyl group in 8,13-dichloro-1,2,3,4-tetrafluoro-9-methyltriptycene (2).



1: X = H, Y = F

2: X = Cl, Y = F

3: X = Cl, Y = H

Compound 2, mp $300-301^\circ\text{C}$, was obtained in 21 % yield by reaction of 1,8-dichloro-9-methylantracene (4)⁵⁾ with tetrafluorobenzene generated *in situ* from pentafluorophenyllithium.^{6,7)} In the ^1H NMR spectrum (CDCl_3 , 90 MHz) at room temperature the methyl proton signal appears as a doublet at δ 3.26 with an H-F coupling of 7.0 Hz, reflecting a rapid internal rotation of the methyl group.⁸⁾ The spectrum at -70°C (CD_2Cl_2 , 400 MHz) indicates

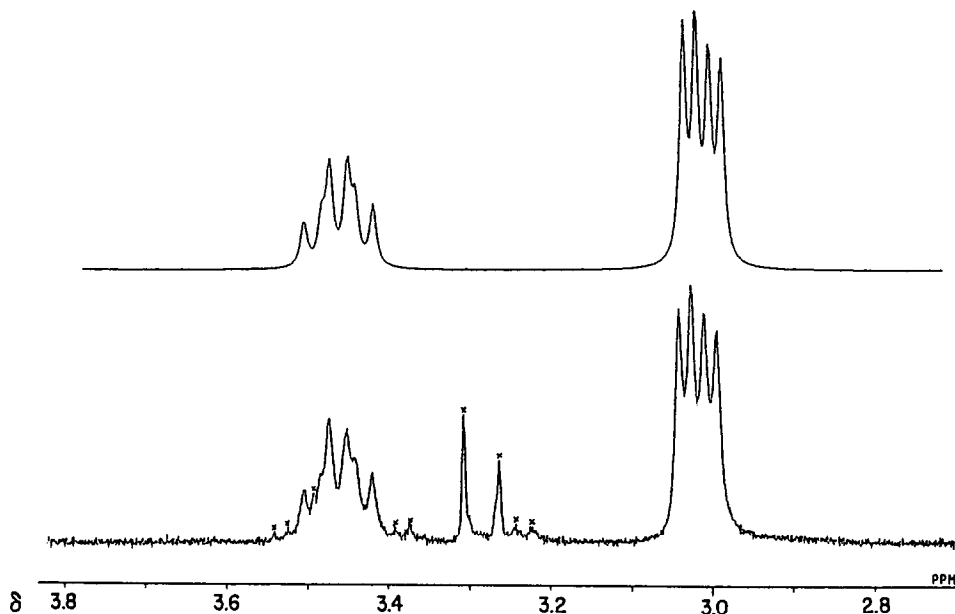


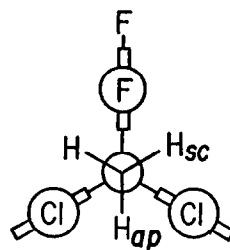
Figure 1. Experimental (lower) and simulated (upper) spectra of the methyl proton region of 2. Signals marked by \times are due to impurities.

the restricted rotation of the methyl group: the methyl signal appears as a two proton double doublet at δ 3.02 ($|\mathcal{J}| = 6.1$ and 12.6 Hz) and a one-proton double triplet at δ 3.46 ($|\mathcal{J}| = 8.7$ and 12.6 Hz) (Fig. 1).

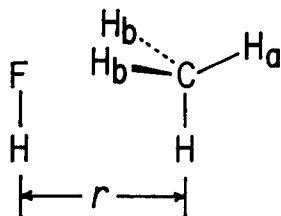
The high-field signal is assigned from its intensity to two s_c protons (H_{sc}), which couple to H_{ap} with 12.6 Hz and further to 1-F with 6.1 Hz,⁹⁾ while the low-field one is due to H_{ap} , which couples to two H_{sc} with 12.6 Hz and to 1-F with 8.7 Hz. The sign of the H-F couplings relative to that of the geminal interproton coupling, which is assumed to be negative, could not be determined even by use of computer simulation (LAOCN3).¹¹⁾ However the averaged coupling of 7.0 Hz observed at room temperature firmly establishes that the two couplings are of the same sign.

Quite intriguing is the fact that 1-F couples to the remote H_{ap} more strongly than to the proximate H_{sc} . Close proximity between the fluorine and the carbon as well as the nearly linear arrangement of $F \cdots C-H_{ap}$ ¹⁴⁾ suggests that the interaction between the lone pair orbital on the fluorine and the rear lobe of the $C-H_{ap}$ bond orbital¹⁵⁾ should be responsible for the large coupling by H_{ap} .

In the ^{13}C NMR spectrum of 2 at ambient temperature¹⁷⁾ the methyl carbon shows a coupling of 12.2 Hz with 1-F, while the 9-carbon does not show a splitting due to C-F coupling. This indicates that the couplings are actually through-space in nature, and further confirms that the electrons belonging to the methyl carbon orbitals participate in the F- H_{ap} coupling.



Wasylishen and Barfield³⁾ made INDO-FPT calculations on a methane-hydrogen fluoride system, in which CH₄ and HF molecules are arranged as shown and H-F coupling constants were



calculated for each proton as a function of the C...F distance x . Stereochemical relations of H_a and H_b with F in this system are very similar to those of H_{ap} and H_{sc}, respectively, with 1-F in 2. For $x = 2.7 \text{ \AA}$, which is the distance between 1-F and the methyl carbon in 2 obtained by molecular mechanics calculations,¹¹⁾ the above calculation predicts H-F couplings of 5.5 and -1.0 Hz for H_a and H_b, respectively. Although the absolute values are considerably different from the observed ones, the tendency that the remote proton couples with F more strongly than the proximate one is reproduced by the calculation if the positive sign is assumed for the observed couplings. Now that the experimental data are at hand, more sophisticated theoretical considerations are desirable.

Presence of interaction between the lone pair orbital on F and the C-H_{ap} bond orbital is expected to result in other consequences which are detected by NMR spectroscopy. Such an interaction, which is considered to be a through-space version of the $n - \sigma^*$ interaction¹⁸⁾ usually postulated between a lone pair orbital and a neighboring σ bond in antiperiplanar arrangement, would increase the electron density around H_{ap} and that would cause the upfield shift of the H_{ap} chemical shift.

In order to ascertain this point by comparing the chemical shift data of 2 with those in the absence of such an interaction, we examined the low temperature ¹H NMR spectrum of 1,8-dichloro-9-methyltriptycene (3). Compound 3, mp 338-340 °C, was obtained by reaction of 4 with benzyne generated *in situ* from anthranilic acid.⁷⁾

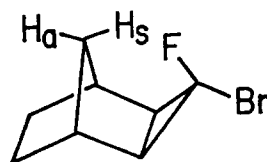
At -70 °C in CD₂Cl₂, where the internal rotation of the methyl group is sufficiently slow, the 400 MHz ¹H NMR spectrum of 3 shows a two-proton doublet at δ 2.75 ($|J| = 12.6 \text{ Hz}$) and a one-proton triplet at δ 3.70 ($|J| = 12.6 \text{ Hz}$). Therefore, while H_{sc} in 2 gives its signal at lower field by 0.27 ppm than H_{sc} in 3, H_{ap} in 2 appears at higher field by 0.24 ppm than H_{ap} in 3.

The downfield shift of the H_{sc} signal in 2 relative to that in 3 may be caused by a combination of the electronegativity and the anisotropy (and/or electric field) effects of the fluorine atoms. The electronegativity effect of the fluorines will be practically the same for both H_{sc} and H_{ap}. The anisotropy (and/or electric field) effect of the fluorines should be greatly reduced because of the long distance in the case of H_{ap}. No significant geometrical difference was found between 2 and 3 by molecular mechanics calculations, and thus the effect of *e.g.* the chlorine atoms would be the same in 2 and 3. Therefore, the upfield shift of H_{ap} on going from 3 to 2 seems to be best explained in terms of $n - \sigma^*$ interaction. Further study along this line is in progress.

Acknowledgment: The authors are grateful to Dr. G. Izumi of Nippon Kayaku Co., Ltd. for the measurements of 400 MHz ^1H and 100 MHz ^{13}C NMR spectra.

REFERENCES AND NOTES

- 1) J. Hilton and L. H. Sutcliffe, *Progr. N. M. R. Spectrosc.*, 10, 27 (1975).
- 2) G. Yamamoto and M. Ōki, *J. Org. Chem.*, 49, 1913 (1984).
- 3) R. E. Wasylishen and M. Barfield, *J. Am. Chem. Soc.*, 97, 4545 (1975). See also: M. Barfield, S. R. Walter, K. A. Clark, G. W. Gribble, K. W. Haden, W. J. Kelly, and C. S. Le Houllier, *Org. Mag. Res.*, 20, 92 (1982).
- 4) M. Nakamura, M. Ōki, and H. Nakanishi, *J. Am. Chem. Soc.*, 95, 7169 (1973); M. Nakamura, M. Ōki, H. Nakanishi, and O. Yamamoto, *Bull. Chem. Soc. Jpn.*, 47, 2415 (1974). See also: J. E. Anderson and D. I. Lawson, *Chem. Commun.*, 1973, 830.
- 5) J. P. Desvergne, R. Lapouyade, and H. Bouas-Laurent, *C. R. Acad. Sci., Paris, Ser. C*, 270, 642 (1970).
- 6) P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227.
- 7) All new compounds were satisfactorily analyzed.
- 8) ^1H NMR data of 2 (CDCl_3 , 35 °C, 90 MHz): δ 3.26 (3H, d, $J = 7.0$ Hz, CH_3), 5.64 (1H, d, $J = 1.8$ Hz, 10-H), 6.8-7.3 (6H, m).
- 9) That the coupling partner is 1-F is deduced by careful analysis of the ^{19}F NMR spectrum¹⁰⁾ of this compound and also by analogy with the related compounds.²⁾
- 10) ^{19}F NMR data of 2 (CDCl_3 , 35 °C, 84.67 MHz, in ppm downfield from internal C_6F_6): 3.28 (app t, $J = 19$ Hz, 2-F), 4.35 (ddd, $J = 5, 19,$ and 22 Hz, 3-F), 12.04 (dd, $J = 15$ and 22 Hz, 4-F), 20.70 (br, 1-F).
- 11) The calculations were made on a HITAC M-280H computer system at the Computer Center of the University of Tokyo by use of LAOCN3¹²⁾ and MM213¹³⁾ programs.
- 12) A. A. Bothner-By and S. M. Castellano, *QCPE*, No. 111.
- 13) N. L. Allinger and Y. H. Yuh, *QCPE*, No. 395.
- 14) The MM2 calculation affords the $\text{F}\cdots\text{C}-\text{H}_{\text{ap}}$ angle of 160 °.
- 15) This idea was previously suggested by Jefford *et al.*¹⁶⁾ to explain the significant H-F coupling (3.0 Hz) exhibited by H_a in 5.
- 16) C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet, and K. C. Ramey, *J. Am. Chem. Soc.*, 91, 1532 (1969).
- 17) ^{13}C NMR data of the aliphatic carbons in 2 (CDCl_3 , 25 °C, 100.5 MHz): δ 22.99 (d, $J = 12.2$ Hz, CH_3), 47.50 (s, 10-C), 55.82 (s, 9-C). Splitting patterns given are those upon proton noise decoupling.
- 18) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Lett.*, 1964, 2553.



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(Received in Japan 30 October 1984)