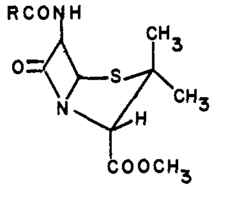
methyl signals results in intensity increases of 13 ± 3% for H_5 only. These results require that H_3 be in spatial proximity to the low-field methyl group (which must therefore be assigned the β orientation) and that H_5 be in spatial proximity to the high-field methyl group (which must therefore be assigned the α orientation). Thus, the thiazolidine ring conformation of the (*R*)-sulfoxides is approximately the same as the conformation of the (*S*)-sulfoxides and considerably different from the conformations of the parent sulfides, **5** and **6**.



5, R = CH_3
6, R = $C_6H_5OCH_2$

The observed shift of 0.80 ppm to higher field for H_5 in going from either of the sulfides **5** or **6** to the corresponding (*R*)-sulfoxides **3** or **4** is unexpected in light of the present concepts of the screening environment associated with the sulfoxide bond.[2,9,10] Since H_5 in the *R* isomers is located in the deshielding region of the sulfoxide bond, a shift to lower field when compared with the same proton in the parent sulfide was expected. Perhaps differences in side-chain conformations originating from differences in intramolecular hydrogen bonding in the sulfoxide isomers play an important role in explaining this anomalous observation. However, lack of quantitative agreement obtained in a recent study[2] as well as qualitative and quantitative discrepancies observed for protons adjacent to the sulfoxide bond in a number of model *t*-butylthiane sulfoxides[11] and 1,4-oxathiane S-oxides[12] suggest that the presently accepted model for the screening environment associated with the sulfoxide bond may be more complicated than previously assumed, especially for protons adjacent to the sulfoxide bond.

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(9) K. W. Buck, *et al.*, *Chem. Commun.*, 759 (1966).

(10) P. B. Sollman, R. Nagarajan, and R. M. Dodson, *ibid.*, 552 (1967).

(11) To be published.

(12) A. B. Foster, *et al.*, *Chem. Commun.*, 1086 (1968).

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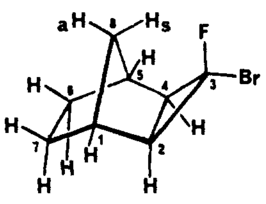
Received October 7, 1968

The Stereochemical Requirements for Proton–Fluorine Spin–Spin Coupling over Five Bonds[1]

Sir:

Numerous cases have been recorded of proton–fluorine spin–spin coupling over five bonds ($^5J_{HF}$). From examination of various fluoro steroids, Cross has formulated the geometric requirement for such coupling as the "converging vector rule." [2] From other examples, it is clear that the magnitude of the coupling is closely related to the internuclear distance between the coupled hydrogen and fluorine atoms.[3–5] Unfortunately, all these cases of $^5J_{HF}$ coupling deal exclusively with methyl protons.[6] Thus, the exact arrangement of the nuclei undergoing interaction is unknown as the particular proton or protons responsible cannot be specified. We now report results obtained from *syn*-3-fluoro-*anti*-3-bromo-*exo*-tricyclo[3.2.1.0^{2,4}]-octane (I) in which the spatial relation of the coupling fluorine and hydrogen atoms is precisely defined by the rigid framework of the molecule.[7]



I

At 94.1 MHz the ^{19}F resonance of I shows as a quintuplet at 146 ppm upfield from trichlorofluoromethane, thereby indicating that the fluorine atom couples to just four protons to about the same extent ($J_{FH} \sim 3.5$ Hz) (Figure 1). It can be reasonably assumed that two of these protons are the vicinal ones on C_2 and C_4.[8] An immediate clue to the identity of the other two is provided by the additional multiplicity displayed by the resonances of the *syn* and *anti* C_8 protons (Figure 2).[9] These additional splittings are unexpectedly large: 3.6 and 3.0 Hz for the *syn* and *anti* protons; moreover, they

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(1) To be regarded as part XIX of a series entitled "The Stereochemistry of Bicyclo[3.2.1]octane." For part XVIII see C. W. Jefford and W. Wojnarowski, *Tetrahedron*, in press.

(2) A. D. Cross and P. W. Landis, *J. Amer. Chem. Soc.*, **86**, 4005 (1964); A. D. Cross, *ibid.*, **86**, 4011 (1964).

(3) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961); M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); D. F. Evans, S. L. Manatt, and D. D. Elleman, *ibid.*, **85**, 238 (1963); M. S. Newman, R. G. Mentzer, and G. Slomp, *ibid.*, **85**, 4018 (1963); A. Lewin, *ibid.*, **86**, 2303 (1964); J. Burdon, *Tetrahedron*, **21**, 1101 (1965); J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

(4) P. C. Myrhe, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, **88**, 2459 (1966).

(5) This statement is based on ref 4. However, the relationship is open to question when dissimilar systems are being compared as the effect of substituents on J_{HF} is unusually large and is not well understood (*cf.* ref 8).

(6) A solitary case dealing with methylene protons constitutes an apparent exception to both the converging vector and the proximity rules (A. B. Foster, R. Hems, L. D. Hall, and J. F. Manville, *Chem. Commun.*, 158 (1968).

(7) Compound I is a product obtained by the action of fluorobromocarbene on norbornene (C. W. Jefford and D. T. Hill, manuscript submitted for publication); proton nmr spectra of the *anti*-chloro analog of I (L. Ghosez, G. Slinckx, M. Glineur, P. Hoet, and P. Laroche, *Tetrahedron Lett.*, 2773 (1967)) were examined and found to be in agreement.

(8) The present value of $^3J_{HF}$ is small compared with that reported for the structurally similar 1-chloro-1-fluoro-2,2-diphenylcyclopropane ($^3J_{HF}$ = 6.3 Hz: K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, **88**, 5678 (1966)) and *exo*-7-bromo-*endo*-7-fluoronorcarane ($^3J_{HF}$ = 13.0 Hz; T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *ibid.*, **89**, 5719 (1967)). However, $^3J_{HF}$ is notoriously sensitive to substituents (C. W. Jefford, D. T. Hill, and K. C. Ramey, paper submitted for publication).

(9) It will be seen from Figure 2 that only a portion of the AB pattern for the *syn* C_8 is observable as the upfield branch is obscured by overlap with other resonances. Nevertheless the assignment is assured by a knowledge of the shielding experienced in the *exo*-tricyclo[3.2.1.0^{2,4}]-octane skeleton (C. W. Jefford and R. T. Medary, *Tetrahedron*, **23**, 4123 (1967)).

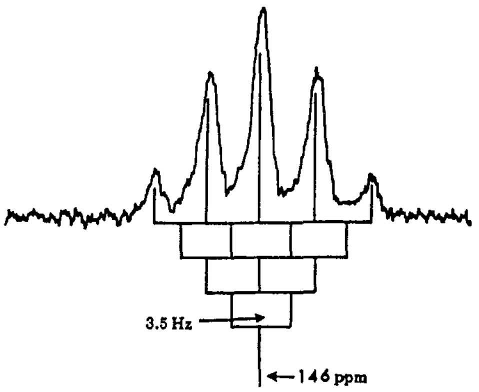

Figure 1. The spectrum of compound I at 94.1 MHz in trichlorofluoromethane.

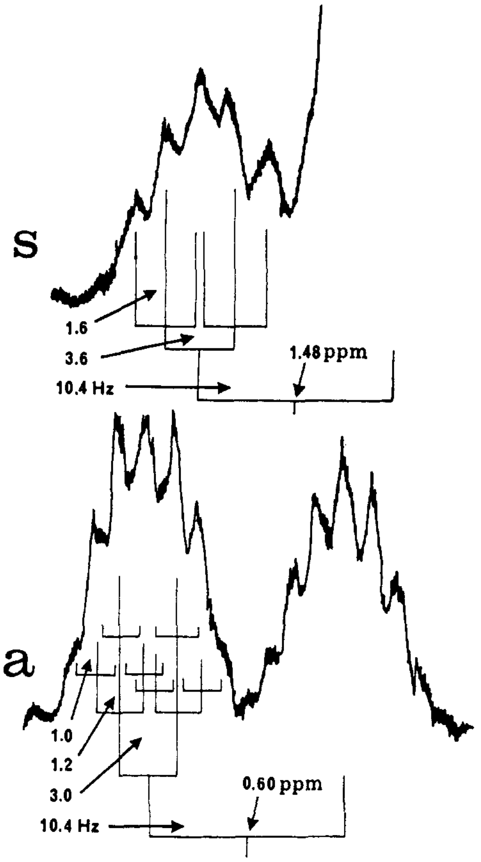

Figure 2. Appearance of the resonances of the C_8 *anti* (a) and *syn* (s) protons of compound I at 100 MHz and at 100-Hz sweep width in deuteriobenzene.

clearly do not correspond to any of the proton–proton arrangements found in the norbornane skeleton.[10] Clarification of the C_8 proton signals was obtained by proton spin decoupling.[11]

Irradiation of the protons on C_1 and C_5 (the bridgeheads) removed the 1.6- and 1.2-Hz couplings from the signals of the *syn* and *anti* C_8 protons leaving a broadened doublet 3.0 Hz wide and a doublet of narrow triplets 3.6 Hz wide, respectively. The residual triplet structure ($^4J_{HH}$ = 1.2 Hz) of the *anti* proton undoubtedly arises from the usual long-range coupling with the W-disposed pair of *endo* protons on C_2 and C_4. On the other hand, the scarcely observed $^4J_{HH}$ couplings of the *syn* proton reflects the poor W geometry of the *endo* protons on C_6 and C_7.[12]

The inescapable finding which emerges is that *both* the *syn* and *anti* C_8 protons are coupled with the fluorine atom and that the two coupling constants are not remarkably different in size ($^5J_{HF}$ = 3.6 and 3.0 Hz, respectively).

The molecular structure of I dictates that the *syn* C_8 proton and the fluorine atom are certainly very close. Indeed, inspection of a model of I puts the internuclear distance at about 1.5 to 1.6 Å, which is less than the sum of the van der Waal's radii of the two atoms.[13,14] It is expected, however, that some of this nonbonded interaction will be alleviated by a separating of the C_8 and C_3 atoms. If the form of the nmr spectra is any guide, this flexion is expected to take place so as to conserve the C_s symmetry of I.

From these findings and considerations, two important conclusions can be drawn. First, the size of $^5J_{HF}$ for the contiguous nuclei is much smaller than expected. For *syn*-diaxially disposed methyl and fluorine groups on a cyclohexane ring in steroids, the values for $^5J_{HF}$ vary between 2.5 and 7.0 Hz, yet the internuclear distances between hydrogen and fluorine are fairly constant, namely of the order of 1.6 and 2.5 Å for the opposed and intercalated conformations of the methyl group (Figure 3a,b).[2,14] Similarly, 2,4,6-tri-*t*-butylfluorobenzene, where the internuclear distances are about 1.95 and 2.25 Å for the two conformations, has $^5J_{HF}$ equal to 7.4 Hz.[4] It should be remembered that these molecules display averaged values of $^5J_{HF}$ as the methyl group is still free to rotate, and further the actual conformation adopted probably lies somewhere between the extremes. Nevertheless, even assuming the closest proximity, these values of $^5J_{HF}$ are appreciably larger than those exhibited by compound I. Accordingly, it can be concluded that the interaction between the *syn* C_8 hydrogen and fluorine atoms occurs by a through space mechanism. It may be that too intimate a contact, as encountered in compound I, results in a diminution of coupling. However, substituent effects could also be responsible for the feebleness of the coupling.[5,8]

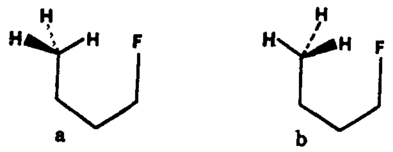

Figure 3. Opposed (a) and intercalated (b) conformations of a methyl group with respect to a fluorine atom.

The second, rather surprising finding is that the *anti*

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[10] K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, **89**, 2401 (1967); A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

[11] Proton decoupling was effected by the frequency-sweep method (*cf.* C. W. Jefford and K. C. Ramey, *Tetrahedron*, **24**, 2927 (1968).

[12] A. Rassat, C. W. Jefford, J.-M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964).

[13] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

[14] Distances were measured on Framework Molecular Models, Prentice Hall, Inc., Englewood Cliffs, N. J.

proton, although directed away from the fluorine, also couples with it. Coupling could conceivably occur through the bonds, but it seems more likely that spin information is relayed either through the agency of the *syn* proton or by overlap of the fluorine with the small rear lobe of the *anti* C_8–H bond.[15] Whatever the mechanism, it is now certain that the satisfaction of the space criterion for a proximal proton will ensure that the geminal, apotropic proton couples as well. Consequently, for the cases of $^5J_{HF}$ coupling involving methyl groups, it has to be considered probable that *all* three methyl protons are simultaneously coupled. It remains to be seen whether other fixed proximal arrangements, for example, that shown by Figure 3b, which do not obey Cross's rule, also undergo coupling through space.

Acknowledgment. We thank the National Science Foundation for the award of a fellowship to one of us (D. T. H.).

(15) This mechanism is reminiscient of that postulated for coupling through oxygen; K. C. Ramey and J. Messick, *Tetrahedron Lett.*, 4423 (1965); F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 5249 (1965).

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Nuclear Magnetic Resonance Spectra of the Dianions of Anthracene and Other Polynuclear Aromatic Hydrocarbons

Sir:

We report here the nmr spectra of a series of dianions obtained by two-electron reduction of planar aromatic hydrocarbons[1] and note some anomalies which arise in an attempt to compare empirically estimated electron densities in these species with those in the corresponding radical anions.

Nmr spectra[2] of the dianions of anthracene (**1**), tetracene (**2**), acenaphthylene (**3**), fluoranthene (**4**), and perylene (**5**), prepared by reduction of the hydrocarbons in tetrahydrofuran-d_8 with metallic sodium or lithium, are shown in Figure 1. Chemical shift data taken from these spectra are summarized in Table I. In all compounds studied, electron exchange[3] broadened the nmr lines of the parent hydrocarbon into the base line as soon as a visually detectable amount of the highly colored radical anion was formed. The spectrum of the dianion appeared only when essentially quantitative two-electron reduction had been achieved.

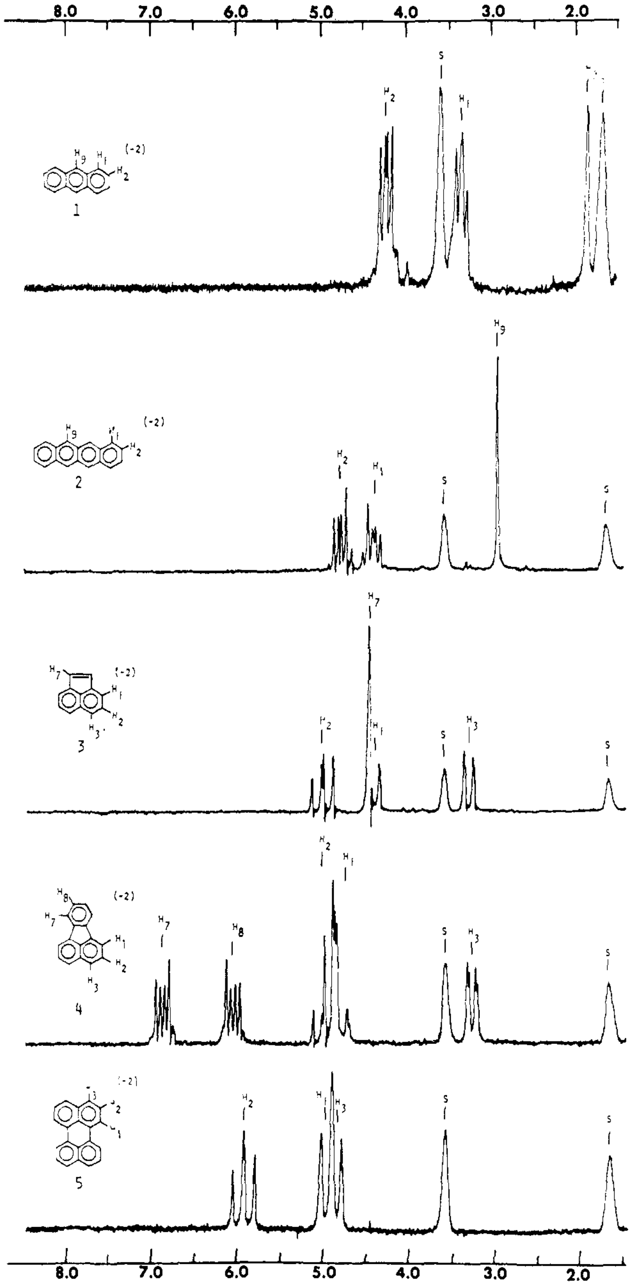

Figure 1. 60-MHz nmr spectra of aromatic hydrocarbon dianions in tetrahydrofuran-d_8. The counterion is lithium in **1** and sodium in all other spectra. Peaks at 1.7 and 3.6 ppm indicated by S arise from the protons in tetrahydrofuran-d_7 present in the deuterated solvent.

The differences in charge-induced chemical shift[4] between protons in the dianions and in their neutral precursors are shown in Table I. The excess charge,

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(1) (a) G. J. Hoijtink, *Rec. Trav. Chim.*, 74, 1525 (1955); (b) G. J. Hoijtink, P. Balk, and J. W. H. Schreurs, *ibid.*, 76, 813 (1957).

(2) All spectra were obtained at 37 ± 1° using an A-60A spectrometer purchased with funds from the National Science Foundation.

(3) (a) E. deBoer and H. van Willigen, *Progr. NMR Spectros.*, 2, (1967). (b) Both uniform and nonuniform broadening of the lines of the neutral and dianionic species have been observed depending on whether the conditions for "strong" or "weak" exchange are met.[3a] In the weak pulse limit, broadening is least for protons such as H_2 and H_7 in fluoranthene and H_2 in perylene which are weakly coupled to the unpaired electron in the radical anion. Further aspects of these electron-exchange effects are currently being investigated.

(4) (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 82, 5846 (1960); (b) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (c) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963); (d) T. J. Katz, *J. Amer. Chem. Soc.*, 82, 3784 (1960); (e) W. G. Schneider in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 63.