downfield shift of the anomeric proton for the latter. This shift is attributed to the close proximity of the anisotropic carbonyl group. The same effect has been observed in other nucleosides with similarly oriented carboxamide substituents.[10]

Spatially the relationship of the ribose ring to the base protons of classes A and B is similar to the situation for H_6 and H_5 of pyrimidine nucleosides. We have observed a $|J_{H_3-H_{1'}}|$ of $\sim$0.6 Hz for class B but not class A compounds in agreement with the findings of Hruska[11] for uridine, 2'-deoxyuridine, and others, provided the anti conformation is assumed.

At a given concentration of added purine, the H_3 resonances of class B compounds were shifted to a higher field than the H_5 resonance of class A compounds which is similar to the case for H_5 and H_6 of pyrimidine nucleosides.[12] This is due to the greater overlap with a costacked diamagnetic purine ring at the proton furthest from the glycosylation site. Finally, assignment of the structure of 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide (virazole) was confirmed by single-crystal X-ray studies by Prusiner and Sundaralingam.[13]

The use of nmr, especially ^{13}C, provides a general unequivocal method for the assignment of structures of highly substituted heterocyclic ring compounds which exhibit very little uv absorption. The efficiency of this method may be extremely advantageous in lieu of more tedious direct chemical procedures.

Acknowledgment. We thank Mr. E. B. Banta for technical assistance and Drs. R. J. Pugmire and Sunney I. Chan for helpful discussions.

[10] G. R. Revankar and L. B. Townsend, *J. Heterocycl. Chem.*, 7, 1329 (1970).

[11] F. E. Hruska, *Can. J. Chem.*, **49**, 2111 (1971).

[12] M. P. Schweizer, S. I. Chan, and P. O. P. Ts'o, *J. Amer. Chem. Soc.*, 87, 5241 (1965).

[13] P. Prusiner and M. Sundaralingam, personal communication.

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Nuclear Magnetic Resonance Studies of Long-Range Carbon-13 Spin Couplings

Sir:

Carbon-13 nuclear magnetic resonance spectroscopy is rapidly becoming an important probe in determining molecular structure. Although many data have been accumulated relating the factors that influence the chemical shift of carbon-13 nuclei,[1] much less is known about the factors that affect the magnitude of the spin–spin coupling constants. This is especially true of long-range carbon-13 spin interactions with fluorine.

In order to gain insight into the spin coupling mechanisms which contribute to carbon-13 nuclear spin coupling, a series of bridged biphenyls was examined. This system was chosen because of its proven utility in assessing the importance of through-space interactions in long-range coupling between H–F and F–F nuclei.[2] It was further hoped that the stereochemical dependence demonstrated in the bridged biphenyls for H–F and F–F coupling would prove useful in understanding $^{13}C-^{19}F$ spin interactions. We now wish to report that carbon-13 nuclei do exhibit long-range coupling to fluorine and that the coupling displays the same stereochemical dependence as observed in H–F and F–F long-range coupling.

The 15.1-MHz $^{13}C-\{^1H\}$ proton noise-decoupled spectrum of 1,4,8-trimethyl-5-fluorophenanthrene (**1**-CH_3) exhibits three methyl carbon resonances at 20.0, 20.2, and 24.0 ppm in addition to aromatic carbon resonances.[3,4] The 24.0-ppm peak exhibits a $^{13}C-^{19}F$ coupling constant of 24.0 Hz and is assigned to the C_4 methyl carbon. This extraordinarily large five-bond $^{13}C-^{19}F$ coupling provides the first compelling evidence that a through-space mechanism can be operative in carbon-13 coupling.[5] Saturation of the 9,10 bond, as in *cis*-1,4,8-trimethyl-5-fluoro-9,10-dihydro-9,10-phenanthrenediol (**2**-CH_3), results in a marked decrease in this coupling constant: $^5J_{C-F} = 15.7$ Hz.[6,7] Oxidation of **1**-CH_3 to 1,4,8-trimethyl-5-fluoro-9,10-phenanthrenequinone (**3**-CH_3) resulted in a similar decrease in the coupling constant: $^5J_{C-F} = 16.1$ Hz. These coupling constants as well as those reported earlier for H–F and F–F couplings in the bridged biphenyl system are summarized in Table I.

Dreiding models of **1**-CH_3, **2**-CH_3, and **3**-CH_3 indicate that severe steric interactions between the groups at the 4 and 5 positions result in large deviations from planarity. This effect is reflected in the chemical shift of the methyl carbons at the four position (*vide infra*).[8] As a result of differences in torsional strains, deviations

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[1] (a) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 7445 (1969); (b) A. J. Jones, D. M. Grant, M. W. Winkley, and R. K. Robins, *ibid.*, 92, 4079 (1970), and references therein.

[2] K. L. Servis and F. R. Jerome, *ibid.*, **93**, 1535 (1971).

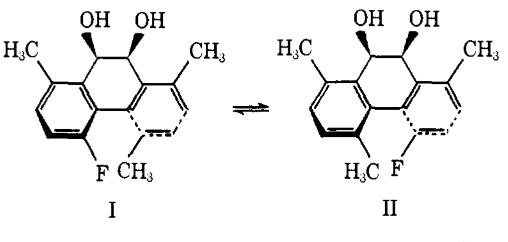
[3] The authors express their appreciation to Dr. Douglas Dorman at the California Institute of Technology for obtaining this spectrum.

[4] (a) The syntheses of **1**-CH_3, 2-CH_3, **3**-CH_3, and **4**-CH_3 have been reported previously; see ref 2. (b) ^{13}C chemical shifts are reported in parts per million downfield from internal tetramethylsilane. **1**-CH_3 was measured in dioxane with dioxane as internal standard. **2**-CH_3 and **3**-CH_3 were measured in chloroform with reference TMS as internal standard. The conversion to reference TMS was made by the assumption: $\delta_{\text{TMS}}^{\text{ref}} = \delta_{\text{dioxane}}^{\text{ref}} - 69.0$ ppm.

[5] (a) The largest previously reported five-bond $^{13}C-F$ coupling was less than 1 Hz: F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2361 (1971). (b) Typical values for geminal $^{13}C-^{19}F$ coupling constants are 20–40 Hz: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 962.

[6] We would like to thank Dr. William Jankowski of Varian Associates for obtaining the ^{13}C nmr spectra of 2-CH_3 and 3-CH_3.

[7] The ^{13}C nmr spectrum of 2-CH_3 displayed very broad absorptions for the methyl carbons at the 1 and 8 positions. This appears to be due to the slow interconversion of the two diastereomeric forms I and II.

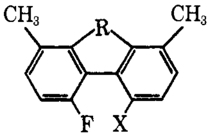


I II

The slow interconversions also result in the observation of two different fluorine resonance absorptions of unequal intensities at 31.26 and 32.86 ppm upfield from 1,1,1-trichloro-2,2,2-trifluoroethane in the 94.1-MHz nmr spectrum.

[8] This effect is also reflected in the ^1H nmr spectra. As the molecule deviates from planarity, the methyl group at the 4 position moves into the positive cone of the other aromatic ring and an upfield shift of the methyl hydrogens results ($\delta_{4\text{-}CH_3}{}^{2\text{-}CH_3} - \delta_{4\text{-}CH_3}{}^{1\text{-}CH_3} = 0.37$ ppm).

Table I. Coupling Constants for Derivatives of 4,5-Difluoro- and 4-Methyl-5-fluorophenanthrenes[a,b]



Compd type	R	X = F; J_{F-F}, Hz	X = CH$_3$; J_{H-F}, Hz	X = CH$_3$; J_{C-F}, Hz	$(J_{F-F})/170$	$(J_{H-F})/11.9$	$(J_{C-F})/24.0$
1	HC=CH	170	11.9	24.0	1	1	1
2	HOCHCHOH	92.9	7.6	15.7	0.55	0.64	0.65
3	O=CC=O	106.5	8.1	16.1	0.63	0.67	0.67
4	O=COC=O	46.7	3.7	(∼7)[d]	0.28	0.30	(∼0.30)[e]
5	O=C	(∼85–100)[d]	7.3[c]	(∼15)[d]	(∼0.61)[e]	0.61	(∼0.61)[e]

[a] Determined from ^{1}H, ^{19}F, and ^{13}C nmr spectra at various spectrometer frequencies. [b] All coupling constants are reported in hertz. [c] Value obtained from the literature: G. W. Gribble and J. R. Douglas, Jr., *J. Amer. Chem. Soc.*, **92**, 5764 (1970). [d] Predicted coupling constants. [e] The same ratio as was observed from H–F couplings was assumed.

from planarity should be smaller for the parent phenanthrene **1**-CH$_3$ than its derivatives, **2**-CH$_3$ and **3**-CH$_3$. The consequence should be a greater proximity of atoms at positions 4 and 5. The proximity of the 4-methyl to the 5-fluoro group seems to produce a downfield shift of the methyl carbon in **1**-CH$_3$ relative to **2**-CH$_3$ and **3**-CH$_3$ ($\delta_{4\text{-C}}{}^{1\text{-CH}_3} - \delta_{4\text{-C}}{}^{2\text{-CH}_3} = 3.4$ ppm; $\delta_{4\text{-C}}{}^{1\text{-CH}_3} - \delta_{4\text{-C}}{}^{3\text{-CH}_3} = 3.2$ ppm).[9]

The changes in proximity of the groups at the 4 and 5 positions are also reflected in changes in the fluorine coupling constants. It was previously demonstrated[2] that the decrease in J_{F-F} can be taken as a standard fractional decrease in through-space coupling as a consequence of this structural variation, $J_{F-F}{}^{2\text{-F}}/J_{F-F}{}^{1\text{-F}} = 0.55$. The observation that ^{13}C–F coupling decreases by a comparative amount, $J_{C-F}{}^{2\text{-CH}_3}/J_{C-F}{}^{1\text{-CH}_3} = 0.64$, implies that through-space interactions contribute substantially to the 4-carbon–5-fluorine coupling constant. This conclusion is reinforced by comparing the ratios $J_{F-F}{}^{3\text{-F}}/J_{F-F}{}^{1\text{-F}} = 0.63$ and $J_{C-F}{}^{3\text{-CH}_3}/J_{C-F}{}^{1\text{-CH}_3} = 0.67$. Furthermore, the observation that H–F coupling and ^{13}C–F coupling decrease by proportionately the same amount permits the prediction of coupling constants in related compounds. For example, using the observed ratio $J_{H-F}{}^{4\text{-CH}_3}/J_{H-F}{}^{1\text{-CH}_3} = 0.30$ leads to a prediction for the ^{13}C–F coupling constant in **4**-CH$_3$ of ∼7.0 Hz. Similarly, the ^{13}C–F coupling in **5**-CH$_3$ is predicted to be ∼15 Hz.

The fact that the ratios of H–F couplings and ^{13}C–F couplings are essentially identical supports our earlier proposal that the coupling between methyl hydrogen and fluorine may result from interactions centered on the fluorine and methyl carbon rather than on the fluorine and hydrogen nuclei.[10,12] Further studies of fluorine coupling in these and related systems are currently in progress and will be reported shortly.

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[9] This downfield shift appears to arise from paramagnetic deshielding of the carbon resulting from proximity of the group at the 5 position. A similar deshielding effect was observed for the fluorine resonances in 1,8-dimethyl-4,5-difluorophenanthrene; ref 2.

[10] This might contribute to the unusual dihedral angle dependence of H–F coupling in *o*-alkylfluorobenzenes.[11]

[11] The α-H–F coupling in *o*-alkylfluorobenzenes appears strongest when the α-H is not proximate to fluorine: P. C. Myhre, personal communication.

[12] A similar through-oxygen coupling has been proposed: F. A. L. Anet, A. J. R. Brown, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 5249 (1965).

[13] National Science Foundation Trainee, 1968–1970; National Aeronautics and Space Administration Fellow, 1970–1971.

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The Claisen Rearrangement of Allyl Esters[1]

Sir:

The recent investigations of Rathke[2] have made possible the generation of ester enolates free of complicating condensation reactions. The possibility that the enolate anions formed from allyl esters under these conditions would undergo a Claisen-type rearrangement on warming has fascinating consequences for both the scope and general applicability of this useful sigmatropic reaction. While the base-catalyzed rearrangement of a few allyl esters has been previously observed,[3] the harsh conditions, low yields, and specialized character of the esters belie the generality of the process. Current investigation of the reaction under these new conditions has resulted in efficient means for the conversion of allyl esters to the corresponding γ,δ-unsaturated acids under surprisingly mild conditions.

Representative examples of a series of the simplest, and hence most demanding, esters are presented in Table I. The esters **1**, **2**, and **5** of tertiary and secondary acids rearranged rapidly at room temperature or slightly above as their lithium enolates, but the acetates **3** and **4** rearranged sufficiently slowly under these conditions that undesired side reactions (aldol-type condensation, ketene formation?) became predominant. Particularly in these cases it was found advantageous to quench the lithium enolate at −78° with trimethylsilyl chloride[4] before warming. The resulting ketene acetals now rearrange quite rapidly. A small amount (2–6%)

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[1] The support of this work by the National Science Foundation is gratefully acknowledged.

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[3] R. T. Arnold and C. Hoffman, *Syn. Commun.*, **2**, 27 (1972), and earlier work; S. Julia, M. Julia, and G. Linstrumelle, *Bull. Soc. Chim. Fr.*, 2693 (1964).

[4] Y. Kuo, F. Chen, C. Ainsworth, and J. J. Bloomfield, *Chem. Commun.*, 136 (1971).