Table I

Starting imide	Nucleophiles (all in DMF)	% yield of products (isolated)		
		Olefin	Substitution	Leaving group
IIa	I$^-$	1-Hexene, 31	*n*-Hexyl iodide, 19	75
	$C_6H_5NH_2$		N-Hexylaniline, 76	84
IIb	I$^-$	1-Hexene, 0–1.5	*n*-Hexyl iodide, 79	
	Br$^-$		*n*-Hexyl bromide, 60	
IIIa	I$^-$	Cyclohexene, 90		93
	$C_6H_5NH_2$	Cyclohexene, 40	N-Cyclohexylaniline, 31	83
IIIb	I$^-$	Cyclohexene, 90		

results in respect to isolated yields are included in Table I.

Preparative samples of the alkenes and the hexyl halides were obtained *via* glpc and/or fractional distillation. The hexyl iodide was sensitive to decomposition under many attempted glpc runs, but pure samples were obtained on a $^3/_8$ in. × 20 ft 30% SF-96 column at 190°. The analytical glpc retention times of all reported liquids were identical with the glpc retention behavior of the authentic reagent grade samples Similarly the ir, nmr, and mass spectra of the product liquids were essentially identical with the corresponding spectra of the authentic samples. The melting point and ir spectrum of the *p*-toluenesulfonimide leaving group were identical with the corresponding data for the imide prepared by another method. The N-hexylaniline was characterized *via* its *p*-tosyl derivative, mp and mmp 67–68° (lit.[4] mp 67–68°) and *via* its ir and nmr spectra. Satisfactory elemental analyses were obtained on starting imides IIa,b and IIIa,b.

Typical runs were conducted as follows. Sulfonimide IIb (0.050 mol) and KI (0.10 mol) were dissolved in 75 ml of DMF and stirred at 110–120° for 2.5 hr. Immediate bulb-to-bulb, high-vacuum distillation of the product, followed by the addition of 50 ml of water to the distilled material, extraction with hexane, washing with water, drying over molecular sieves, and vacuum distillation, gave 0.0395 mol (79%) of pure hexyl iodide as indicated by homogeneous glpc behavior and the spectral analyses. The leaving group derived from sulfonimide IIb is apparently unstable under the reaction conditions, but acidification and recrystallization of the nonvolatile N,N-di-*p*-toluenesulfonimide from a similar run with sulfonimide IIa gave 75% of material which melts at 168–170° (lit.[5] mp 169°). Sulfonimide IIIb was treated similarly at 90° for 41 hr to give 90% of cyclohexene. The cyclohexene was isolated by fractional distillation. The runs with bromide anion and aniline were conducted in a similar manner.

The reaction of IIa and IIIa with aniline constitutes a new technique for obtaining N-alkylanilines. This reaction may eventually prove to be generally useful for the synthesis of secondary amines. Preliminary results also indicate that cyanide and hydroxide anions react with these sulfonimides. The yields with the cyanide and hydroxide nucleophiles have thus far been poor. Further investigations relating to the synthetic possibilities as well as to the mechanistic details of all these reactions are currently in progress.

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Anisotropic Nuclear Spin–Spin Coupling in Methyl Fluoride

Sir:

We wish to report evidence for anisotropic indirect nuclear spin–spin coupling in methyl fluoride. Previous nmr spectral studies of the fluoromethanes[1–3] partially oriented in a liquid crystal[4] showed no evidence for anisotropic contributions to the *geminal* indirect spin–spin interactions. When a sample of CH_3F enriched with 55% ^{13}C is examined, an unexpectedly large apparent anisotropy in the ^{13}C–H and ^{13}C–F indirect coupling is found as described below. Possible reasons for the large values of the measurements are discussed.

The spin-Hamiltonian for molecules partially oriented in a magnetic field is[5]

$$\mathcal{H} = -(H_Z/2\pi)\sum_i \gamma_i(1 - \overline{\sigma_{ZZi}})I_{Zi} + \sum_{i<j} J_{ij}\mathbf{I}_i\cdot\mathbf{I}_j + \frac{1}{2}\sum_{i<j}(\overline{T_{ZZij}} + \overline{J_{ZZij}} - J_{ij})(3I_{Zi}I_{Zj} - \mathbf{I}_i\cdot\mathbf{I}_j)$$

where the bars denote averages over the molecular motion with respect to the space-fixed axis Z. The total anisotropic coupling is composed of two parts. One contribution, $\overline{J_{ZZij}} - J_{ij}$, is the averaged anisotropy in the electron-coupled spin–spin interaction

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Table I. Experimental Spectral Splittings and Anisotropic Indirect Spin-Spin Interactions Determined from the Proton and ^{19}F Magnetic Resonance of CH_3F in Nematic *p,p'*-Di-*n*-hexyloxyazoxybenzene at 80°[a]

Interaction	Spectral splitting	Isotropic coupling J_{ij}[b]	Total anisotropic coupling D_{ij}	Direct coupling $\overline{T_{zz_{ij}}}$	Anisotropic indirect coupling $(J_\parallel - J_\perp)_{ij}$
^{1}H H-H	501.7 ± 1.0	. . .	+334.5	+334.5	0[c]
H-F	222.2 ± 0.6	+46.3 ± 0.3	−268.5	−268.3	−18 ± 54
C-H	422.4 ± 0.9	+148.8 ± 0.4	+273.6	+252.7	+1890 ± 130
		S_{zz} = +0.01657			
^{19}F H-F	222.9 ± 0.4	+46.3 ± 0.3	−269.2	−269.0	−18 ± 54
C-F	509.0 ± 0.8	−161.9 ± 0.7[d]	−347.1	−354.9	+700 ± 130
		S_{zz} = +0.01661			

[a] Values in hertz. The error limits reflect the precision of measurement. [b] Measured in the isotropic phase at 140°. [c] Assumed zero. [d] J_{C-F} = 162.1 ± 0.2 in the gas phase measured at room temperature.

and, experimentally, cannot be distinguished from the other contribution, the averaged direct nuclear spin-spin interaction, $\overline{T_{zz_{ij}}}$. The failure of the spectral analysis to distinguish between the two interactions makes the determination of $\overline{J_{zz_{ij}}} - J_{ij}$ dependent upon a knowledge of the molecular geometry since $\overline{T_{zz_{ij}}}$ is proportional to $\langle 1/r_{ij}^3 \rangle$. For axial molecular symmetry $\overline{J_{zz_{ij}}} - J_{ij} = {}^2/_3 S_{zz}(J_\parallel - J_\perp)_{ij}$, where S_{zz} is a parameter that describes the average orientation of the molecular symmetry axis with respect to the applied magnetic field, and $(J_\parallel - J_\perp)_{ij}$ is the anisotropy in the indirect spin-spin coupling tensor with respect to the molecular symmetry axis.

The experimentally determined total anisotropic spin coupling, direct plus indirect, $D_{ij} = (\overline{T_{zz_{ij}}} + \overline{J_{zz_{ij}}} - J_{ij})$, for the different internuclear interactions in $^{13}CH_3F$ are listed in Table I. Previous analysis of the ^{12}C compound revealed that the anisotropy in the H-F indirect coupling was zero within experimental error if it was assumed that the proton-proton interaction arose only from the direct dipole-dipole interaction.[1,3] This result, also observed in the other fluoromethanes,[3] is apparent in Table I where an assumption of $(J_\parallel - J_\perp)_{HH} = 0$ leads to a calculated H-F direct coupling of −268.3 Hz which agrees well with the observed coupling of −268.5 Hz. The difference, which is less than experimental error, could be due to the presence of an anisotropic H-F indirect interaction as indicated in Table I. However, the calculated ^{13}C-H direct interaction is 20.9 Hz less than the observed interaction, which yields $(J_\parallel - J_\perp)_{CH} = +1890 + 130$ Hz. The ^{19}F spectrum, observed under conditions where the H-F splitting is nearly identical with that observed in the proton spectrum, yields an apparent ^{13}C-F spin coupling anisotropy of $(J_\parallel - J_\perp)_{CF} = +700 \pm 130$ Hz. While the anisotropy in the indirect spin-spin interaction might be expected to be larger for nuclei directly bonded to one another than for *geminal* nuclei, the values encountered here are unexpectedly large.

Several assumptions have been made in the above determination of the anisotropic ^{13}C-H and ^{13}C-F indirect spin coupling. First, the indirect proton-proton coupling is assumed completely isotropic. The spectra of *all* the fluoromethanes, CH_3F, CH_2F_2, and CHF_3, can be interpreted with zero anisotropy in all *geminal* indirect interactions. Introduction of an anisotropic H-H indirect coupling would require an introduction of a concomitant anisotropic H-F indirect coupling. That these be equal and opposite for all the fluoromethanes seems unlikely. A second assumption is the validity of the use of the infrared and microwave geometry[6] in the interpretation of the nmr spectra. Microwave and infrared spectral geometries are derived from $\langle 1/r_{ij}^2 \rangle$ while the direct dipole-dipole interactions are proportional to $\langle 1/r_{ij}^3 \rangle$. For a given vibrational state, r_{ij} derived from $\langle 1/r_{ij}^2 \rangle$ is not exactly equal to r_{ij} derived from $\langle 1/r_{ij}^3 \rangle$. In addition, the two lowest vibrational modes of methyl fluoride (1046.0 and 1197.7 cm^{-1})[6] each have an excited state population of approximately 1.5% at 80°, the temperature of the present experiment. Excited state population and anharmonicity in the vibrational potential may also influence the apparent molecular geometry.

It remains to be seen whether a reasonable change in apparent geometry can account for the unusually large indirect spin-spin coupling anisotropies. Preliminary results[7] show that it is possible to find a geometry such that either the C-H or C-F spin-spin coupling anisotropy vanishes. However, it has not been possible to make both anisotropic contributions vanish simultaneously. If $(J_\parallel - J_\perp)_{CH}$ is set to equal zero then $(J_\parallel - J_\perp)_{CF}$ changes from +700 to −1000 Hz, and if $(J_\parallel - J_\perp)_{CF}$ is set to zero then $(J_\parallel - J_\perp)_{CH} = +1100$. The most prominent geometrical effect that accompanies these imposed anisotropies is the change in the HCF bond angle from the microwave and infrared value of 108.95[6] to 107.67°, when $(J_\parallel - J_\perp)_{CH} = 0$ or to 108.35° when $(J_\parallel - J_\perp)_{CF} = 0$.

Further consideration of possible anharmonic vibrational contributions to the direct dipole-dipole coupling may influence the magnitude of the experimentally deduced spin-spin coupling anisotropies, but all considerations indicate this anisotropy can be much larger than previously anticipated.

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