# Magnetic non-equivalence of fluorine atoms of a trifluoromethyl group

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The three fluorine atoms of N, N-dialkyl amide and chloride derivatives of 2-methoxy-2-phenyl-3,3,3-trifluoropropanoic acid are magnetically nonequivalent below  $-60^{\circ}$ C and exhibit a clear ABC coupling pattern from which chemical shifts and geminal coupling constants are readily derived. The chemical shifts span a range of about 10 ppm and the geminal coupling constants average about 110 Hz. A five bond coupling of about 5 Hz is observed between the hydrogens of the methoxy group and one of the nonequivalent fluorine atoms of the trifluoromethyl group. Barriers to the hindered rotation about the single bond to the trifluoromethyl group are in the range 36–46 kJ/mol.

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Les trois atomes de fluor du N,N-dialkylamide et du chlorure provenant de l'acide méthoxy-2 phényl-2 trifluoro-3,3,3 propanoique sont magnétiquement non équivalents en dessous de  $-60^{\circ}$ C et présentent un modèle clair de couplage ABC duquel on déduit facilement les déplacements chimiques et les constantes de couplage géminal. Les déplacements chimiques s'étalent sur un intervalle de 10 ppm environ et les constantes de couplage géminal sont en moyenne de 110 Hz environ. On observe un couplage à travers 5 liaisons de 5 Hz environ entre les hydrogènes du groupe méthoxy et l'un des atomes de fluor non équivalent du groupe trifluorométhyle. Les barrières à la rotation encombrée autour de la liaison simple du groupe trifluorométhyle sont de l'ordre de 36 à 46 kJ/mol.

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#### Introduction

Fluorine nmr is an important technique in structural determination because of the extreme range (~800 ppm) of chemical shifts that are observed. <sup>19</sup>F chemical shifts and coupling constants have been used extensively to derive conformational and configurational information, much of it, however, in compounds in which the fluorine atoms are attached to rigid ring systems. In conformationally mobile systems, some information is lost due to averaging over structures, a consequence of the relatively long time scales of nmr experiments. Frequently, however, specific information may be obtained at temperatures at which conformation or group exchanges are slow on the nmr time scale.

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The nmr spectral measurements of diastereomeric ester and amide derivatives of 2-methoxy-2-phenyl-3,3,3-trifluoropropanoic acid 1 have been



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routinely used for the determination of absolute configurations and optical purities of chiral alcohols and amines, after the pioneering work of Mosher and co-workers (1, 2). The esters, 3, and amides of primary amines, 4 ( $R^1 = H$ ), each display a single sharp fluorine resonance and mixtures of configurationally diastereomeric compounds often have separated signals for the ---CF<sub>3</sub> groups, rendering assessment of relative abundances by integration facile. The conformational (or geometric) diastereoisomerism of which each of 3 and 4 ( $R^1 = H$ ) is capable, namely (Z)-3  $\rightleftharpoons$  (E)-3 and (Z)-4  $\rightleftharpoons$  (E)-4, is not evident in the ambient temperature nmr spectrum. Either the rate of interconversion is sufficiently rapid to average the signals of the geometric diastereomers or the equilibrium favours one of the isomers to the virtual exclusion of the other.



The former is unlikely, since it is known that rotation about the carbon-nitrogen bond of amides, including amides from primary amines (3), is hindered by a barrier of about 67-92 kJ/mol (3, 4). The corresponding barriers in esters are probably somewhat lower. For simple acetates and formates, barriers in the range 42-55 kJ/mol have been obtained by *ab initio* computations (5). Acyclic esters exist preferentially in the Z-conforma-

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tion, (Z)-3 (6, 7) which is at least 7.6 kJ/mol (the value for tert-butyl formate (7)) more stable than the E-conformer. Ab initio computations have yielded values in the range 17-35 kJ/mol in favour of the Z-form, e.g. (Z)-3, over the E-form, e.g. (E)-3, for methyl formate and methyl acetate (5, 8, 9). For amides of primary amines, the situation is similar. The carbon-nitrogen backbone in proteins has the Z-configuration, and simple acyclic Nmonoalkyl amides also adopt the Z-conformation to the virtual exclusion of the other except in the case of formamides (10). For more complex Nmonoalkyl amides, and for N,N-dialkyl amides, it is generally agreed that minimization of steric repulsions is the single most important factor which leads to a preference of one conformation over the other (11, 12) and this should be the case for 4 also.



Amides of chiral secondary amines, e.g. 4 ( $\mathbb{R}^1 \neq \mathbb{R}^2 \neq H$ ), present complications for the determination of absolute configurations or optical purities which arise from the fact that, in general, pairs of geometric diastereomers as well as configurational diastereomers are evident in the <sup>1</sup>H nmr spectrum (13, 14), at ambient temperature. Indeed, the room temperature <sup>19</sup>F nmr spectrum of amide 5, pre-



pared in connection with another study, shows two broad, unequal, overlapping absorptions. While multiple absorptions in the <sup>19</sup>F nmr spectrum were expected, the breadth of the lines was not. We present below the analysis of several derivatives of 1, namely 2, 6-8, in which nmr spectral changes are attributed to unusually high barriers to hindered rotation about the carbon-carbon single bond to the trifluoromethyl group.





#### Experimental

#### Materials

Dimethylamine, diisopropylamine, and 2,6-dimethylpiperidine were commercial reagent grade, and were redistilled before use and their purity checked by glc (Porapak Q). The 2,6dimethylpiperidine (Aldrich Chemical Co.) is the *cis*- or (*R*,*S*)isomer as verified by <sup>13</sup>C nmr spectroscopy (14). No trace of the *trans*- or (*d*,*l*)-isomer is detectable in the ambient temperature <sup>13</sup>C spectrum.

#### 2-Methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (2) (α-Methoxy-α-trifluoromethylphenylacetyl chloride)

Racemic and  $(+)-\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetic acids (Aldrich Chemical Co.) were converted to the corresponding acid chlorides by a modification of the published procedure (1) using a catalytic amount of dimethylformamide (15).

#### Preparation of (±) and (+)-2-methoxy-2-phenyl-3,3,3trifluoropropanamides

(a). The amides of ammonia (4,  $R^1 = R^2 = H$ ) and dimethylamine (6) were prepared according to the general procedure of Mosher (1) and were characterized by <sup>1</sup>H nmr spectroscopy. Samples were diluted with the appropriate solvent for the <sup>19</sup>F nmr spectroscopy experiments.

(b). The amides of diisopropylamine (7) and 2,6-dimethylpiperidine (8) required heating with the acid chloride for 3 h (reflux) followed by standing at room temperature for 18-20 h. The amides were characterized by <sup>1</sup>H nmr and samples were diluted with the appropriate solvent for the <sup>19</sup>F nmr experiments.

#### Nuclear magnetic resonance experiments

The <sup>19</sup>F nmr spectra were recorded at 188.1 MHz on a Varian XL-200 spectrometer, equipped with a variable temperature controller (accurate to  $\pm 1^{\circ}$ C). All spectra were referenced against TFA (trifluoroacetic acid) in CDCl<sub>3</sub> and converted to the  $\vartheta$  scale (16) using the conversion factor:  $\vartheta = \vartheta_{TFA} - 76.1 \text{ ppm}$ . For the temperature range  $+60^{\circ}$ C to  $-65^{\circ}$ C, CDCl<sub>3</sub> was used as the solvent; for the range  $-60^{\circ}$ C to  $-128^{\circ}$ C, CFCl<sub>3</sub> was used as the solvent and the instrument was run unlocked, using the same machine frequencies employed in the locked spectra and assuming no field drift.

#### Results and discussion

## Low temperature <sup>19</sup>F nmr spectrum and parameters of the trifluoromethyl group

The temperature dependence of the <sup>19</sup>F nmr spectrum of 6 is typical of that of the other compounds and is shown in Fig. 1. At 22°C there is a single, somewhat broadened, resonance at  $\delta = -71.3$  ppm. Upon lowering the sample temperature, the signal broadens considerably and disappears at about -50°C, the coalescence temperature in both CDCl<sub>3</sub> and CFCl<sub>3</sub>. At lower temperatures (CFCl<sub>3</sub>) the signal reappears and sharpens into an ABC coupling pattern at -100°C. The observations must be due to hindered rotation about the C—CF<sub>3</sub>

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FIG. 1. The <sup>19</sup>F nmr spectra of **6** in the temperature range 23°C to  $-100^{\circ}$ C. Rate constants were determined by lineshape fitting using DNMR3 (ref. 22). The spectra at the two lowest temperatures were recorded in CFCl<sub>3</sub>, the rest in CDCl<sub>3</sub>.

bond. The <sup>19</sup>F nmr spectral data of 6, as well as 2, 7, and 8, are given in Table 1. We refer to the individual fluorine resonances as  $F_A$ ,  $F_B$ , and  $F_C$ where  $F_A$  is at highest frequency and  $F_C$  at the lowest.

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The nmr spectral data of all of the compounds of Table 1 have the following features in common. The <sup>1</sup>H nmr shows a five bond coupling, <sup>5</sup>J<sub>HF</sub> = 2Hz, between the CF<sub>3</sub> group and the protons of the methoxy group. The long range coupling is highly stereospecific since only the middle fluorine (F<sub>B</sub>) resonance displays broadening due to the (unresolved) coupling in the <sup>19</sup>F spectrum when CF<sub>3</sub> rotation is slow on the nmr time scale. In the case of 7, the low temperature proton spectrum was recorded down to  $-80^{\circ}$ C. The signal of the methoxy protons, initially a quartet, <sup>5</sup>J<sub>HF</sub> = 1.9 Hz, undergoes coalescence and then sharpens into a doublet, <sup>5</sup>J<sub>HFB</sub> = 4.7 Hz. Since (<sup>5</sup>J<sub>HFA</sub> + <sup>5</sup>J<sub>HFB</sub> + <sup>5</sup>J<sub>HFC</sub>)/3 = 1.9 Hz, neither <sup>5</sup>J<sub>HFA</sub> nor <sup>5</sup>J<sub>HFC</sub> can exceed 1 Hz, thus confirming the stereospecificity of the long-range coupling to a single fluorine atom.

The average CF<sub>3</sub> chemical shift of all of the compounds is  $-70.2 \pm 0.5$  ppm at low temperature. The narrowness of the observed range suggests that the local electronic and magnetic environment of the CF<sub>3</sub> group is similar in all cases. The median chemical shift difference  $\langle \delta F_A - \delta F_C \rangle$  is 10.3 ppm  $\pm$  1.2 ppm. All of the observed geminal coupling constants  ${}^2J_{\rm FF}$  are in the range 111  $\pm$  8 Hz. For each compound the same pattern is observed, namely  $J_{\rm AC} > J_{\rm AB} > J_{\rm BC}$ . Individual fluorine resonances arising from

Individual fluorine resonances arising from restricted rotation about a single bond to a trifluoromethyl group have been previously reported, first in 2,2,3,3-tetrachloro-1,1,1,4,4,4-hexafluorobutane (17) and then other halo alkanes (18, 19) and in several trifluoromethyl substituted phosphoranes (20, 21). The chemical shifts and coupling constants reported in Table 1 for derivatives of **1** are similar to those previously observed in the perhaloalkanes, although in the latter compounds, the chemical shift differences between the individual fluorine atoms of the CF<sub>3</sub> group are somewhat larger, 12–16 ppm (17–19).

### Barriers to the hindered rotation

From the limiting values of chemical shifts and coupling constants, given in Table 1, and the temperature dependence of the lineshapes of the <sup>19</sup>F signals (e.g. 6, Fig. 1), activation parameters were obtained for 2, 6, and 7 using the computer programme DNMR3 (22*a*) for rate constants. In each case, satisfactorily straight lines were obtained in a plot of ln (k/T) vs. 1/T.

[1] 
$$k = \left(\frac{k_{\rm B}}{h} T\right) e^{-(\Delta H^{\pm} - T\Delta S^{\pm})/RT}$$

 $\Delta H^{\pm}$  and  $\Delta S^{\pm}$  were obtained from the "least squares" lines. Free energies of activation,  $\Delta G^{\pm}$ ,

Compound	Chemical shifts (ppm) <sup>a</sup>			Coupling constants (Hz)				Activation parameters		
								$\Delta G^{+}$	$\Delta H^{\dagger}$	 ΔS <sup>‡</sup>
	$\partial F_{A}$	∂F <sub>B</sub>	$\partial F_c$	$J_{\rm AB}$	$J_{AC}$	$J_{\rm BC}$	$T_{\rm c}(^{\circ}{\rm C})$	kJ/mol	kJ/mol	J/mol-deg
20	-65.97	-70.33	-75.12	112.5	113.9	109.4	-90	$33.0 \pm 0.1'$	$34.2 \pm 1.3'$	6.3±7.4'
<b>6</b> <sup>c</sup>	-66.09	-72.26	-75.67	108.9	117.1	106.1	-50	$40.46 \pm 0.01^{g}$	35.8±0.5°	$-21.0\pm2.4''$
7	-64.95	-71.64	-74.68	107.8	118.1	106.4	-10	$47.25 \pm 0.04^{h}$	$44.1 \pm 0.5^{h}$	$-11.8\pm2.2^{h}$
<b>8</b> a <sup>e</sup>	-65.00	-71.96	-75.09	109.6	113.4	107.8	-20	ACI		
$8b^{e}$	-63.92	-70.20	-75.43	107.5	118.3	104.9		40		

TABLE 1. <sup>19</sup>F nuclear magnetic resonance parameters and CF<sub>3</sub> rotation barriers for derivatives of 1

"Values ( $\partial$ ) are cited relative to CFCl<sub>3</sub> (16). The relative values are accurate to the level of significance shown. <sup>a</sup>In CFCl<sub>3</sub> at -128°C. <sup>c</sup>In CFCl<sub>3</sub> at -100°C.

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"In CPC1<sub>3</sub> at -10.5"C. "In CDC1<sub>3</sub> at -63.5"C. "Relative abundance 8a/8b = 2.0, in CDC1<sub>3</sub> at -63°C. These correspond to the geometric isomers which arise from rotation about the amide C(O)—N bond. "Temperatures (°C) and rate constants (s<sup>-1</sup>): -60, 45000: -80, 4900; -100, 225; -110, 92; -115, 37; -120, 16.5. "Temperatures (°C) and rate constants (s<sup>-1</sup>): 0, 60 000; -20, 18 500; -40, 4000; -60, 540; -65, 390; -80, 65. "Temperatures (°C) and rate constants (s<sup>-1</sup>): 21, 20 000; 0, 5200; -20, 1020; -40, 142; -50, 56; -55, 27. 'Estimated using the Eyring equation (see text),  $k_c \approx 1700 \, \text{s}^{-1}$ .

were obtained at the coalescence temperature  $T_c$ , using eq. [2]. Errors were estimated using eq. [3], following Binsch and Kessler (22b).

 $[2] \quad \Delta G^{+} = \Delta H^{+} - T_{c} \Delta S^{+}$ 

[3] 
$$\sigma(\Delta G^{\dagger}) \approx |\sigma(\Delta H^{\dagger}) - T\sigma(\Delta S^{\dagger})|$$

The results are given in Table 1. For 8, lineshape analysis could not be used because the low temperature <sup>19</sup>F spectra are complicated due to the presence of geometric (rotational) diastereomers. These occur as a consequence of rotation about the C(O)—N bond. The free energy of activation for 8 was estimated from the Eyring equation (eq. [4]), where an approximate rate constant,  $k_c$ , at the coalescence temperature,  $T_{\rm c}$ ,

$$[4] \quad k_{\rm c} = \left(\frac{k_{\rm B}}{h} T_{\rm c}\right) {\rm e}^{-\Delta G^{\ddagger}/RT_{\rm c}}$$

was obtained using DNMR3 and average limiting chemical shifts taken from Table 1. The values so obtained for 8 are:  $\Delta G^{+} = 46 \text{ kJ/mol}, T_{c} = -20^{\circ}\text{C},$  $k_{\rm c} = 1700 \, {\rm s}^{-1}$ .

Barriers to hindered rotation about C-C single bonds have been the subject of several reviews (3, 23). Barriers to rotation about bonds of the  $sp^3-sp^3$ type range from 11.7 kJ/mol (for ethane) to values as high as 140 kJ/mol, generally increasing with the size of the substituents. Barriers to rotation about bonds terminating in the CF<sub>3</sub> group are generally in the range 16-35 kJ/mol (17) (16.4 kJ/mol for  $CF_3CF_3$  (24). Values obtained in the present study (Table 1) are somewhat higher than the norm but consistent with the high coalescence temperatures observed, and reflect the severe steric crowding of the substituents at the chiral centre. Indeed it is very difficult to prepare a spacefilling model of any of the compounds 2–8.

### Stereochemistry of the individual fluorine resonances

It would be of interest to assign the individual fluorine resonances in the chiral environment of the derivatives of 1. Although an unambiguous assignment cannot be made at this time, several facts are consistent with the assignment shown in structure 9, where  $F_A$  is at highest frequency and X is Cl or a



 $-NR^{1}R^{2}$  group. In each of the compounds listed in Table 1, the individual fluorine atoms of the trifluoromethyl group are separated by about 10 ppm. <sup>19</sup>F chemical shifts have been related to the covalency of the bonding to fluorine and to the anisotropy of the charge distribution of the fluorine atom. A shift to low field (deshielding) due to the paramagnetic contribution is greatest in covalently bonded fluorine and is zero in the spherically symmetric F<sup>-</sup> ion (25). Although explicit calculation of the chemical shifts of fluorines in systems such as 1-8 is beyond our present capabilities, in order to obtain a measure of the amount of covalent character of the bonds to the three fluorine atoms, we have performed extensive geometry optimization by the MNDO method (26) on one of the conformers of 6, shown below, which we judged from construction of spacefilling models most likely to correspond to the global minimum. Beginning with  $\theta_1 = 0^\circ$  and  $\theta_2 = -60^\circ$ , and optimizing a total of 34 independent structural parameters (bond lengths, bond angles, and dihedral angles (only the internal geometry of the three methyl groups and

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the phenyl ring were constrained to standard values), the structure relaxed to  $\theta_1 = 1^{\circ}$  (CF<sub>3</sub> groups eclipsed to carbonyl group) and  $\theta_2 = -50^{\circ}$ . The calculated anisotropies (27), L(X), of the three fluorine atoms and bond orders (27), B(C,F), of the bond to the fluorine atom can be used as indicators of covalent character. The calculated quantities for the three fluorine atoms (structure 9) are  $L(F_A) = 0.3458$ ,  $L(F_B) = 0.3425$ ,  $L(F_C) = 0.3404$ ,  $B(C,F_A) = 0.9347$ ,  $B(C,F_B) = 0.9289$ , and  $B(C,F_C) = 0.9253$ . Although the differences in anisotropy and bond order appear to be small, direct application of the observed (25) correspondence between chemical shift and covalency yields the result that  $F_A$  should be at highest frequency and  $F_C$  at lowest.



The above result is consistent with the assignment of  $F_B$  as the fluorine atom which is coupled to the protons of the methoxy group. The computations show the closest contact to be between  $F_B$  and the methyl group,  $r(F_B--CH_3O) = 2.50 \text{ Å}$ , compared to  $r(F_A--CH_3) = 4.24 \text{ Å}$  and  $r(F_C--CH_3O) =$ 3.18Å. The observed 5-bond F-H coupling is reminiscent of the stereospecific 5-bond F-F coupling reported by Weigert and Roberts (17), which was ascribed to "through space" or "direct" coupling, a mechanism which has substantial experimental support (28, 29). Although Weigert has urged restraint in the correlation of structure with "through space" coupling constants (19), the observed couplings  ${}^{5}J_{F_{B}-H} = 4.3 \text{ Hz in } 6, {}^{5}J_{F_{B}-H} =$ 4.7 Hz in 7 are very nearly those expected for  $r(F_B - H) = 2.5 \text{ Å}$  using Myhre's curve which relates  $J_{\rm HF}$  to  $r(\rm F--H)$  (29).

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