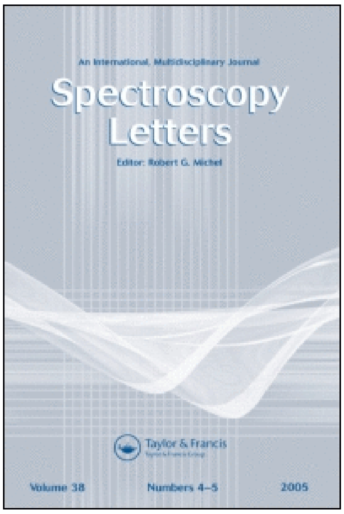

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Natural Abundance ^{17}O NMR Study of Substituted α,α,α-Trifluoromethoxybenzenes

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NATURAL ABUNDANCE ^{17}O NMR STUDY OF SUBSTITUTED α,α,α-TRIFLUOROMETHOXYBENZENES

KEY WORDS: ^{17}O NMR spectroscopy, trifluoromethoxy group

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ABSTRACT

Natural abundance ^{17}O NMR chemical shift data for *meta-* and *para-*substitued α,α,α-trifluoromethoxybenzenes recorded in acetonitrile at 75° C are reported. The ^{17}O NMR signals for the trifluoromethoxy compounds are deshielded by greater than 65 ppm compared to analogous methoxy compounds. A quantitative relationship between ^{17}O NMR chemical shifts for the trifluoromethoxy and methoxy benzenes is reported.

INTRODUCTION

Only recently has the influence of the OCF_3 group on reactivity of aromatic compounds been studied.[1] Comparable systematic studies of the influence of the OCF_3 group as a substituent on spectroscopic properties of aromatic systems have not been reported. Previous spectroscopic work only dealt with selected trifluoromethoxy aryl compounds and includes photoelectron,[2] infrared,[3,4] and ultraviolet spectroscopy[5] studies, as well as ^{19}F and ^{13}C NMR spectroscopy investigations.[6,7]

^{17}O NMR spectroscopy is a sensitive method for evaluation of the influence of structural variation on properties of functional groups containing oxygen atoms.[8-10] Aryl ethers have been extensively studied by ^{17}O NMR spectroscopy.[11-18] The ^{17}O NMR chemical shifts of substituted anisoles are highly sensitive to substituent electronic[12] and steric effects.[13,15,16] ^{17}O NMR studies have not appeared for trifluoromethoxy aryl systems. This report describes the influence of both *meta* and *para* substituents on the ^{17}O NMR chemical shifts of trifluoromethoxybenzene.

RESULTS

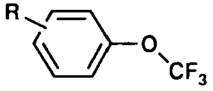
The ^{17}O NMR chemical shift data for the α,α,α-trifluoromethoxybenzenes (**1-11**) recorded at natural abundance in acetonitrile at 75°C are listed in Table 1. The ^{17}O NMR signal for the trifluoromethyloxy group is downfield of that for the methoxy group by approximately 65 ppm; compare the value for **4**, 113.1 ppm with that reported for anisole, 48 ppm.[12] The ^{17}O NMR signal for *para*-substituted OCF_3 compounds range between 106 ppm for the *p*-amino compound **1** and 118 ppm for the *p*-cyano compound **8**. As expected, the chemical shift range (ca. 2 ppm) for the *meta*-substituted compounds **9-11** is greatly compressed. Electron donating groups cause upfield shifts and electron withdrawing groups result in downfield shifts of the trifluoromethoxy ^{17}O NMR signal. The influence of aromatic ring substituents on the trifluoromethoxy ^{17}O NMR signal is similar to that reported for substituted anisoles;[12] however, the chemical shift range is significantly compressed for the trifluoromethoxy series.

DISCUSSION

The ^{17}O NMR chemical shift of the divalent oxygen of the trifluoromethoxy benzenes is influenced by substituents in a manner similar to that reported for

TABLE 1

^{17}O NMR Chemical Shifts of Substituted α,α,α-Trifluoromethoxybenzenes in Acetonitrile at 75°C.[a]



No.	R	δ (-O-)[b]	ν 1/2 (-O-)[c]	δ(x)[d]	ν 1/2 (x)[c]
1	*p*-NH_2	106.2	400		
2	*p*-OH	107.1	420	77.6	435
3	*p*-F	109.6	260		
4	*p*-H	113.1	241		
5	*p*-Br	111.8	349		
6	*p*-CHO	118.0	280	568.6	299
7	*p*-$CONH_2$	114.4	400	327.4	441
8	*p*-CN	118.2	357		
9	*m*-Br	114.5	280		
10	*m*-NH_2	112.7	437		
11	*m*-CN	114.0	330		

a) Data obtained at natural abundance from 0.5 M solutions at 75°C. b) Chemical shift in ppm referenced to external water; 1% 2-butanone (558±1) internal reference. c) Linewidth (Hz) at half peak height. d) Chemical shift (ppm) of oxygen of substituent.

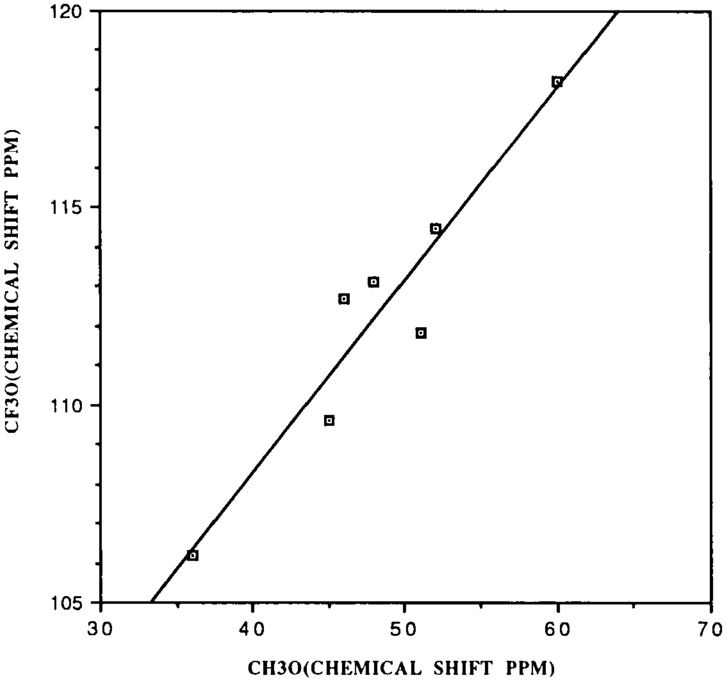


FIGURE 1. PLOT OF O-17 NMR CHEMICAL SHIFTS OF TRIFLUOROMETHOXYBENZENES VS 17-O NMR CHEMICAL SHIFTS OF ANISOLES

anisoles as demonstrated by the linear relationship in the plot presented in Figure 1. The anisole ^{17}O NMR data were correlated[12] with electron density on the oxygen and the chemical shifts were interpreted as being dependent upon the r^{-3} term of the Karplus-Pople expression.[19] The relationship shown in Figure 1 suggests a similar dependency for the chemical shifts of trifluoromethoxy benzenes.

The slope for the line shown in Figure 1, $\delta_{(CF_3O)} = 0.49\delta_{(CH_3O)} + 88.8$ (r=0.95), shows that the CF_3O oxygen is approximately one-half as sensitive to substituent effects as the oxygen of the CH_3O group. The reduction in sensitivity to substituents of the CF_3O ^{17}O NMR signal is consistent with the lower electron density of the oxygen for such groups and is also consistent with the suggestion, based upon photoelectron spectroscopy data, that the CF_3O group is poorly conjugated with aromatic rings.[2] The ^{17}O NMR chemical shift of anisoles is reported to give a good correlation with Hammett sigma minus values.[12] However, the ^{17}O NMR data for the trifluoromethoxybenzene system gives only poor correlations (r = ca. 0.9) with sigma, sigma minus and sigma plus (plots not shown) values.

The ^{17}O NMR spectroscopic results reported here are consistent with the aromatic trifluoromethoxy compounds' lower reactivity in comparison with methoxy analogs, which can be explained by the lower electron density of the oxygen of the former compounds. The large difference (ca. 65 ppm) in ^{17}O NMR chemical shift values between anisoles and trifluoromethoxybenzenes demonstrates the sensitivity of ^{17}O NMR chemical shifts of singly bonded oxygen to structure variation.

EXPERIMENTAL

The compounds used in this study were commercially available from Fairfield Chemical Company.

The ^{17}O NMR spectra were recorded on a Varian VXR-400 spectrometer equipped with a 10 mm broad-band probe. Spectra were acquired at natural abundance, at 75°C in acetonitrile (Aldrich, anhydrous gold label under nitrogen) containing 1% 2-butanone as an internal standard. The concentration of the trifluoromethoxybenzenes employed in these experiments was 0.5 M. The signals were referenced to external deionized water at 75°C. The 2-butanone resonance (558±1 ppm) was used as an internal check on the chemical shift measurements for these compounds. The instrumental settings were: spectral width 35 kHz, 2K data points, 90° pulse angle (40 μs pulse width), 200 μs acquisition delay, 29 ms acquisition time. Typically 15,000-30,000 scans were required. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±0.1 ppm by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be better than ±1.0 ppm.

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