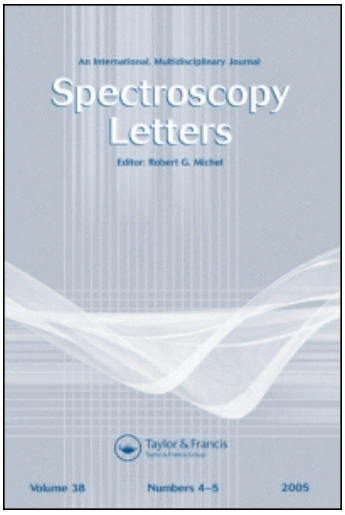

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NATURAL ABUNDANCE ^{17}O NMR STUDY OF HINDERED ARYL ACID CHLORIDES

KEY WORDS: ^{17}O NMR spectroscopy, acid chlorides, torsion angles

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ABSTRACT

Natural abundance ^{17}O NMR chemical shift data for 12 variably hindered aryl acid chlorides recorded in acetonitrile at 75° C are reported. The ^{17}O NMR signals for the hindered acid chlorides are deshielded relative to unhindered isomers. A quantitative relationship between molecular mechanics (MM2) estimated torsion angles and ^{17}O NMR chemical shifts for the aryl acid chlorides is developed.

INTRODUCTION

The ^{17}O NMR chemical shift of a number of types of functional groups have been shown to be dependent on the aryl ring-functional group torsion angle.[1,2,3] The carbonyl ^{17}O NMR signals for aromatic esters and the signals for aromatic carboxylic acids are known to be sensitive to electronic effects[4,5] and quantitative relationships have been found between their ^{17}O NMR chemical shift

and torsion angle values.[6] Other derivatives of carboxylic acids, amides[6,7] and anhydrides[8,9] have been studied by ^{17}O NMR approaches and a quantitative dependency between aryl amide carbonyl group ^{17}O NMR signals and torsion angles have been found.[6,7] Only recently has ^{17}O NMR methodology been applied to a significant number of acid chlorides, the most reactive of the carboxylic acid derivatives.[10,11] Good correlations between ^{17}O NMR chemical shifts and Hammett type relationships for para substituted benzoyl chlorides have been found[10,11] and indicate the importance of resonance effects on acid chloride ^{17}O NMR chemical shift. However, to date no report has appeared which demonstrates the sensitivity of the carbonyl ^{17}O NMR signal of the acid chloride group to torsion angles. This study describes the effect of steric interactions on the carbonyl ^{17}O NMR chemical shift for a series of hindered aryl acid chlorides and develops a quantitative relationship between ^{17}O chemical shift and torsion angle.

RESULTS

The ^{17}O NMR chemical shift data for the aryl acid chlorides (**1-12**) recorded at natural abundance in acetonitrile at 75°C are listed in Table 1. The ^{17}O NMR signal for the acid chlorides range between 485 and 543 ppm. The ^{17}O NMR signal of simple unhindered aryl acid chlorides (e.g., **1** and **9**) appears upfield of typical arylketones; however, as steric interactions are increased, the acid chloride ^{17}O NMR resonance is shifted downfield clearly into the region where aryl ketones and aldehydes absorb.[1] Examination of the ^{17}O NMR chemical shift values for **1**, **6** and **12** shows an increasing chemical shift (485 to 523 to 543 ppm) which parallels increasing repulsive van der Waals interaction between the carbonyl group and adjacent hindering groups.

TABLE 1

^{17}O NMR Data for Aryl Acid Chlorides in Acetonitrile.[a]

No.	Name	δ (C=O)[b]	ν 1/2 (C=O)[c]	TA[d]
1[e]	Benzoyl chloride	485.5	151	0
2[e]	2-Methylbenzoyl chloride	505.5	116	29
3	2,3-Dimethylbenzoyl chloride	510.1	226	38
4	2,4-Dimethylbenzoyl chloride	499.1	190	28
5	2,5-Dimethylbenzoyl chloride	505.1	191	29
6	2,6-Dimethylbenzoyl chloride	523.3	213	62
7	2,4,6-Trimethylbenzoyl chloride	531.2	238	62
8	1-Naphthoyl chloride	505.8	239	47
9	2-Naphthoyl chloride	485.3	286	0
10	2-Methyl-1-naphthoyl chloride	537.1	270	73
11	1-Methyl-2-naphthoyl chloride	512.9	283	48
12	9-Anthroyl chloride	543.3	340	90

a) Data obtained at natural abundance from 0.5 M solutions at 75°C. b) Chemical shift (ppm) referenced to external water; 1% 2-butanone (558±1) internal reference. c) Linewidth (Hz) at half peak height; estimated error 10%. d) Torsion angle estimated by MM2 method. e) Data taken from ref. 11.

DISCUSSION

Previous studies demonstrated good correlations between the ^{17}O NMR chemical shifts of para-substituted benzoyl chlorides and para-substituted acetophenones as well as methylbenzoates.[11] These correlations were considered evidence for the dependency of benzoyl chloride ^{17}O NMR chemical shift on π-electron density of the carbonyl group. In addition, the correlations were interpreted as evidence that the sensitivity to electronic effects for the functional groups as measured by ^{17}O NMR was $COCl \sim COCH_3 > CO_2Me$.[11] A somewhat different analysis leads to similar conclusions but with a slight modification of the order $COCH_3 > COCl > CO_2Me$.[10] It was therefore of interest to compare the sensitivity of these functional groups to steric interactions using ^{17}O NMR methodology. Figure 1 contains plots of the ^{17}O NMR chemical shifts of the hindered aryl acid chlorides vs the data for their counterpart methyl aryl ketones and methyl aryl esters. Both lines in Figure 1 yield reasonably good correlations. The correlations indicate that factors influencing the chemical shifts in the three different systems are proportional. These correlations are consistent with torsion angle rotation to relieve repulsive van der Waals interactions.[2] The downfield shifts for the signals of all three similar functional groups correspond to an increase in double bond character of each carbonyl group.

A quantitative relationship between increasing steric interactions for a reporter functional group and ^{17}O NMR chemical shift was first noted for aryl nitro compounds.[22] Since that report a number of ^{17}O NMR chemical shift-functional group torsion angle relationships have been developed.[3] Representative compounds in the 2-substituted benzoyl chloride family showed large downfield chemical shifts relative to their para-substituted isomers; however, too few hinder benzoyl chlorides were studied to attempt to develop a quantitative relationship.[1]

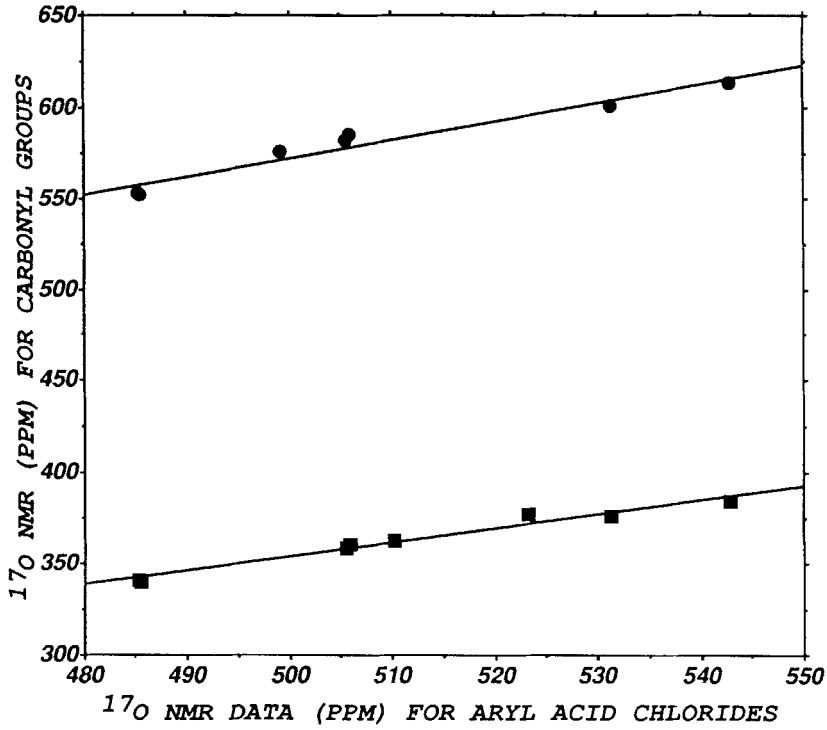

Figure 1. Plot of ^{17}O NMR chemical shifts of aryl acid chlorides vs ^{17}O NMR chemical shifts of aryl methyl ketones (top) and ^{17}O NMR chemical shifts of methyl aryl esters (bottom).

Figure 2 demonstrates the quantitative relationship between ^{17}O NMR chemical shifts and MM2 estimated torsion angles for the aryl acid chlorides. In principle, the electronic effect of the substituent should be taken into account; however, in this study since the contribution to the ^{17}O NMR chemical shift of the hindering groups (alkyl groups) is small, the electronic factor for the alkyl group is neglected. The slope of the line (0.65 ppm/deg) for the acid chloride ^{17}O NMR-torsion angle

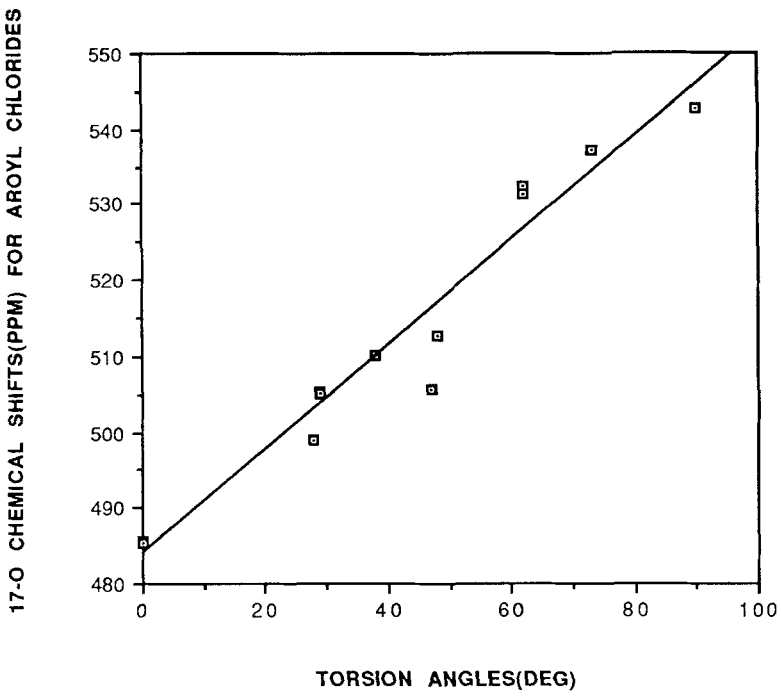

Figure 2. Plot of ^{17}O NMR chemical shifts (ppm) of aryl acid chlorides versus MM2 estimated torsion angles (degrees).

correlation is less than that noted for methyl aryl ketones (0.84 ppm/deg) but similar to that for aryl esters (0.70 ppm/deg).[3,6] The magnitude of the chemical shift-torsion angle slope seems to parallel the double bond character of the functional groups.[3,6]

The ^{17}O NMR chemical shift-torsion angle dependency has been interpreted to be related to the change in electron density of the carbonyl oxygen with change in torsion angle for various other carbonyl containing functional groups.[2,3] It seems likely that this effect is the origin of the downfield shift for aryl acid chlorides. The results described in this report further illustrate the utility of ^{17}O NMR spectroscopy

as a method for evaluation of conformational structure of oxygen containing functional groups. The method is particularly sensitive for functional groups containing double bonded oxygen as illustrated in this report by the data for aryl acid chlorides.

EXPERIMENTAL

^{17}O NMR data for the acid chlorides **1** and **2** have been previously reported.[11] Compound **9** was commercially available from Aldrich. The remaining compounds have been reported previously and were prepared by reaction of the appropriate carboxylic acid with thionylchloride by standard methodology.[12] ^{1}H and ^{13}C NMR data were consistent with the assigned structures; other physical data were in accord with literature values: **3**,[13] **4**,[14] **5**,[15] **6**,[16] **7**,[17] **8**,[18] **10**,[19] **11**[20] and **12**.[21]

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 compounds 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 20,000-50,000 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.

Molecular mechanics calculations were carried out by use of the program MODEL Version KS2.94 available from Professor K. Steliou, University of Montreal.

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