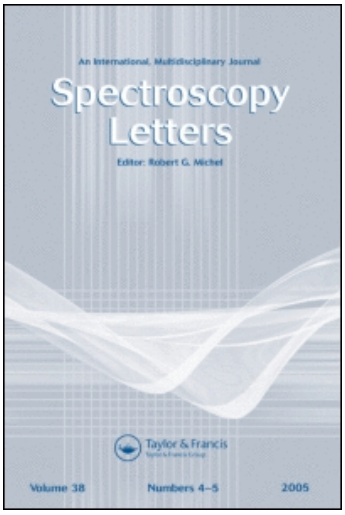

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Natural Abundance ^{17}O NMR Studies on Methyl N-Arylcarbamates: Torsion Angle and Electronic Effects

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NATURAL ABUNDANCE ^{17}O NMR STUDIES ON METHYL N-ARYLCARBAMATES: TORSION ANGLE AND ELECTRONIC EFFECTS

KEY WORDS: ^{17}O NMR spectroscopy, N-Arylcarbamates, torsion angles, electronic effects

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ABSTRACT

Natural abundance ^{17}O NMR data for 14 substituted methyl N-arylcarbamates obtained in acetonitrile solution at 75°C are reported. The ^{17}O NMR chemical shifts of hindered *ortho* N-arylcarbamates are shielded relative to unhindered ones; a quantitative relationship is observed between the carbonyl ^{17}O NMR chemical shifts and molecular mechanics (MM2) predicted torsion angles. The carbonyl ^{17}O NMR chemical shifts of *meta* and *para* substituted N-arylcarbamates are correlated with Hammett sigma constants.

INTRODUCTION

The utility of ^{17}O NMR spectroscopy to assess substituent electronic and steric influences on carbonyl ^{17}O NMR chemical shifts is now well established.[1,2,3] Quantitative relationships between carbonyl ^{17}O NMR chemical shifts and parameters (e.g., Hammet type sigma constants) which describe the electronic properties of substituents have been reported for aryl aldehydes,[4] aryl ketones,[5,6] aryl carboxylic acids,[7] aryl esters,[7] aryl acid chlorides,[8,9] and N-arylacetamides.[10] Also, quantitative relationships have been developed between torsion angle values and ^{17}O NMR chemical shift data for a variety of functional groups[1-3] including

arylamides[11] and N-arylacetamides.[10] It has been demonstrated that the torsion angle-functional group ^{17}O NMR chemical shift relationships are an indirect result of minimization of van der Waals interactions by rotation of the functional group from the plane of the aromatic ring.[3] For most of the systems studied to date as the functional group-aromatic ring torsion angle is increased, the ^{17}O NMR chemical shift increases. The opposite trend has been noted for only two systems, α-diketones[12] and N-arylacetamides.[10] The ^{17}O NMR study of methyl N-arylcarbamates reported herein provides the opportunity for further examination of both the influence of substituent electronic factors and steric interactions on the ^{17}O NMR chemical shift of the carbonyl functional group.

RESULTS

The ^{17}O NMR chemical shift data for the substituted methyl N-arylcarbamates (**1-14**) recorded at natural abundance in acetonitrile at 75°C are listed in Table 1. The carbonyl signal appears in the 240-254 ppm range and the -O-CH_3 signal is found at 97±4 ppm. The carbamate carbonyl signals appear in the region observed for the carbonyl oxygen value for urea (240 ppm) and related uracils.[13] The carbonyl signal of the parent molecule 1 is upfield by 110 ppm of that of N-phenylacetamide.[10] The ^{17}O NMR signal for the carbamate -O-CH_3 group is also upfield by approximately 30 ppm compared to the analogous signal in typical methyl esters.[11] Electron donating groups cause shielding of both the carbonyl and the -O-CH_3 signal and electron withdrawing groups cause deshielding of the two signals. The magnitude of the substituent induced chemical shift change is significantly greater for the carbonyl signal than for the O-CH_3 one. The introduction of substituents *ortho* to the carbamate function results in upfield shifts of the carbonyl ^{17}O NMR signal. The magnitude of the upfield shift produced by *ortho* methyl groups is approximately 5 ppm per methyl group, appears to be additive, and is slightly smaller than the value found for similarly substituted N-phenylacetamides.[10]

DISCUSSION

The fact that the carbonyl ^{17}O NMR signal for carbamates is upfield from that of N-phenylacetamide analogs by greater than 100 ppm indicates greater single bond character for the carbamate carbonyl group, consistent with participation of the carbamate methoxy oxygen in the

TABLE 1

^{17}O NMR Chemical Shift Data for Substituted Methyl N-Arylcarbamates in Acetonitrile at 75°C.

Compound #	*$ArNHCO_2CH_3$*	*Torsion angle (°)*	*δ (C=O)[a] ppm*	*ν/2[b] hz*	*δ (-O-CH_3)[a] ppm*	*ν/2[b] (hz)*	*δ (other)[a,c] ppm*	*ν/2[b] hz*
1	Ph		244.8	272	97.3	321		
2	4-NO_2-C_6H_4		253.9	506	100.9	550	569.0	711
3	3-$CF_3C_6H_4$		248.0	353	98.4	410		
4	3-ClC_6H_4		247.9	317	98.1	325		
5	4-ClC_6H_4		245.7	420	97.2	540		
6	3-MeC_6H_4		244.6	283	95.0	341		
7	4-MeC_6H_4		242.7	320	95.6	330		
8	4-$MeOC_6H_4$		240.6	390	94.9	530	44.7	362
9	2-MeC_6H_4	31	239.7	304	94.7	380		
10	2,6-$Me_2C_6H_3$	60	235.5	381	91.5	298		
11	2,4-$Me_2C_6H_3$	30	238.5	350	93.5	380		
12	2,5-$Me_2C_6H_3$	31	239.3	323	93.8	346		
13	2,6-$Et_2C_6H_3$	70	234.7	481	91.0	500		
14	2,3-$Me_2C_6H_3$	37	238.6	287	94.1	487		

a) Chemical shift in ppm referenced to external water; 1% 2-butanone (558±1 ppm) internal reference.

b) Linewidth (herz) at half peak height. c) Chemical shift of oxygen of substituent.

bonding of the carbonyl group. The methoxy ^{17}O NMR signal is also upfield of that of typical esters, suggesting that for carbamates participation of the nitrogen lone-pair electrons with the carbonyl is significant compared to oxgyen lone-pair involvement and hence that for carbamates the O-CH_3 group is more ether-like than ester-like.

Quantitative relationships between functional group ^{17}O NMR chemical deshielding shifts and torsion angles have been developed for numerous systems.[1-3] Upfield shifts which correlate with torsion angles have been noted for only two systems.[10,12] The plot of carbonyl ^{17}O NMR data versus MM2 estimated torsion angles for six *ortho* alkyl substituted N-arylcarba-

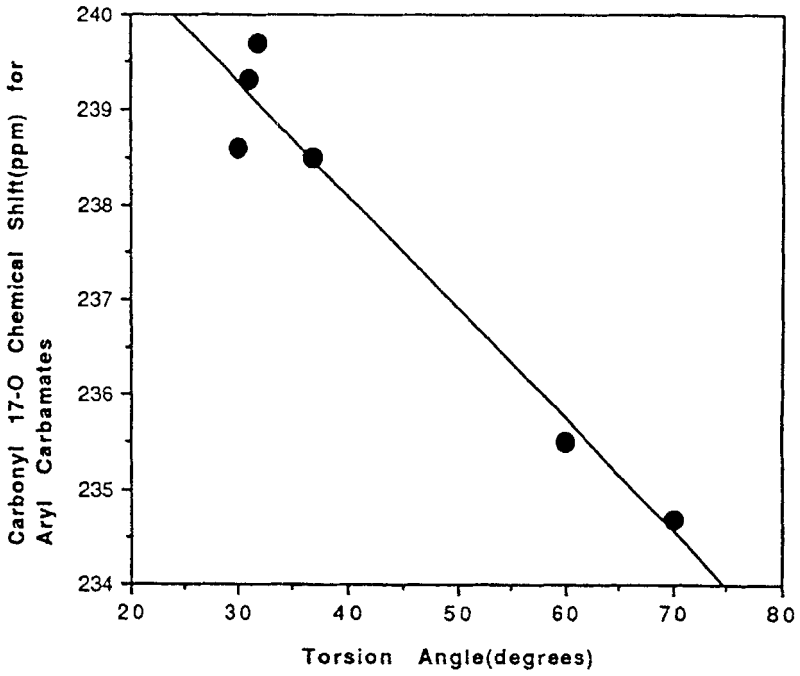

Figure 1. Plot of ^{17}O NMR chemical shifts (ppm) of the carbonyl signal of methyl N-arylcarbamates versus MM2 estimated torsion angles (degrees).

mates is shown in Figure 1. These results represent the third example of a torsion angle-upfield shift relationship. The data plotted in Figure 1 do not include a value for the parent molecule 1. Molecular mechanics calculations for 1 failed to give a reliable value for its torsion angle; values ranging from 1° to 21° were obtained on minimization with no significant differences in total energy. Consequently, the expression for the line in Figure 1 and the observed carbonyl chemical shift for 1 were used to estimate the torsion angle for 1 and a value of 11° was obtained. The upfield shift arising from torsion angle rotation of N-arylacetamides was explained in terms of diminution of aryl-amide nitrogen conjugation with concomitant increase of amide nitrogen-carbonyl group participation. A similar explanation seems appropriate for the N-arylcarbamate results. The slope of the line for the N-arylcarbamate relationship [δ = -0.13 TA + 243.4] -0.13 ppm/deg

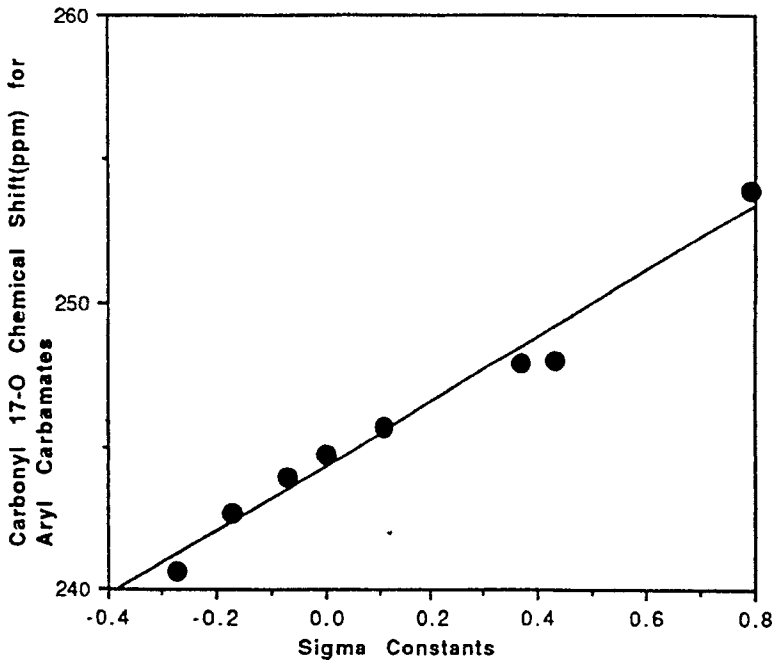

Figure 2. Plot of ^{17}O NMR chemical shifts (ppm) of N-arylcarbamates vs Hammett sigma constants.

is significantly reduced from that for the N-arylacetamide data (-0.36 ppm/deg).[10] These results suggest that aryl-nitrogen conjugation is less for the carbamates than the N-arylacetamides.

The influence of electronic factors on the carbonyl ^{17}O NMR chemical shift of the N-arylcarbamates is rather large; note the difference of 13 ppm for the signal of **2** and **8**. Figure 2 contains a plot of carbonyl ^{17}O NMR data for seven *meta* and *para* substituted N-arylcarbamates and it also includes data for the parent molecule **1**. The correlation between Hammett sigma constants and ^{17}O NMR chemical shift is reasonable and the slope of the line is 11.2 ppm. This value is approximately half the value for the similar relationship observed for N-arylacetamides. Thus, this data also suggests that aryl ring-nitrogen conjugation is not as important in the carbamates as for N-arylacetamides.

The ^{17}O NMR data for N-arylcarbamates were found to be sensitive to both steric and electronic influences of the aryl substituents. As was noted for N-arylacetamides[10] an increased

torsion angle produced upfield shifts for the carbonyl oxygen signal. However, both results from torsion angle analysis and from Hammett analysis suggest that aryl ring-functional group conjugation is significantly reduced in the N-arylcarbamate system. Thus, ^{17}O NMR data can be used to estimate solution phase conformations of hindered N-arylcarbamates and to provide insight into the bonding interaction of the carbamate functional group with the aryl ring.

EXPERIMENTAL

The compounds used in this study were obtained from Aldrich 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 N-arylcarbamates 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 30,000-60,000 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 VersionKS2.94 available from Professor K. Steliou, University of Montreal.

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