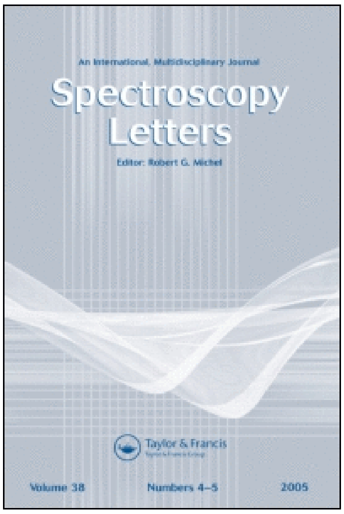

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^{17}O NMR Investigation of Aryl Isocyanates: Electronic and Steric Effects

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^{17}O NMR INVESTIGATION OF ARYL ISOCYANATES: ELECTRONIC AND STERIC EFFECTS

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KEY WORDS: ^{17}O NMR, Aryl isocyanates, Steric and electronic effects

ABSTRACT

The natural abundance ^{17}O nmr spectra of seventeen aryl isocyanates are reported. Electronic effects of substituents are consistent with previously investigated carbonyl containing functional groups; however, the steric effects of ortho-alkyl groups give results which are opposite to those noted for other systems.

INTRODUCTION

Isocyanates are of general interest and wide use in organic synthesis.[1] Their unusual properties are considered a consequence of their cumulated double bonds. Generally, the NCO cumulated system is thought to be linear;[1,2] however, neither the geometry of the NCO group nor, more specifically, the bond angle between nitrogen and the aryl ring for aryl isocyanates has been rigorously determined.[3] Surprisingly, no X-ray data for aryl isocyanates could be found in the literature. Spectroscopic investigations of aryl isocyanates have included limited ^{13}C and ^{15}N nmr studies;[2,4,5] however, no report of the ^{17}O nmr chemical shift of this functional group has appeared. Since ^{17}O chemical shifts are more sensitive to structure variation than ^{13}C and ^{15}N ones and since ^{17}O chemical shifts are proving to be valuable measures of subtle structural changes for a number of functional groups,[6-10] it seemed important to determine the influence of both electronic and steric interactions on the ^{17}O chemical shift of this presumably linear functional group. This communication reports the ^{17}O chemical shifts of series of ortho, para and multi substituted aryl isocyanates.

RESULTS AND DISCUSSION

The ^{17}O nmr data for the aryl isocyanates (**1-17**), determined from 0.5 M solutions at natural abundance in dry acetonitrile at 75°C, are listed in Table 1. The ^{17}O chemical shift of the aryl isocyanate group appears further upfield (100-120 ppm) than any previously reported carbon oxygen double bond system in an organic structure; the alkyl isocyanate signal should be even further upfield. Typical organic carbonyl ^{17}O chemical shifts range from near 600 ppm for certain aldehydes and ketones[6] to near 300 ppm for amides;[6] urea and related compounds appear near 200 ppm.[6] The ^{17}O nmr signal for the isocyanate group which appears near 100 ppm is thus in a distinctive region for carbon-oxygen double bond containing compounds. This result suggests greater single bond character for this carbon-oxygen double bond system than for those with which it has been compared.

The electronic effect on the isocyanate ^{17}O chemical shift is illustrated by examination of the data for the 4-substituted isocyanates (**1, 2, 3, 4, 6, 9, 11, 16**). The chemical shift ranges from 122.8 ppm for the 4-nitro compound **1** to 108.5 ppm for the 4-methoxy compound **16.** The downfield shift for **1, 2, 3** and **4,** relative to **5,** is consistent with an increase in double bond character due to the electron withdrawing substituents; correspondingly, the upfield shift of **6, 9, 11** and **16,** relative to **5,** is consistent with an increase in single bond character resulting from the electron donating substituents. The chemical shift of

TABLE 1

^{17}O Chemical Shift Data for Aryl Isocyanates in CH_3CN at 75°C.

Compound #	Ar	δ(NCO)[a]	δ(other)[a]
1	$4\text{-}NO_2C_6H_4$	122.8	572.2
2	$4\text{-}EtO_2CC_6H_4$	118.4	338.9, 159.2
3	$4\text{-}CF_3C_6H_4$	118.7	
4	$4\text{-}ClC_6H_4$	114.7	
5	C_6H_5	111.3	
6	$4\text{-}CH_3C_6H_4$	109.5	
7	$2\text{-}CH_3C_6H_4$	106.2	
8	$2,6\text{-}DiCH_3C_6H_3$	101.0	
9	$4\text{-}C_2H_5C_6H_4$	110.7	
10	$2\text{-}C_2H_5C_6H_4$	106.3	
11	$4\text{-}iPrC_6H_4$	110.2	
12	$2\text{-}\underline{i}PrC_6H_4$	101.0	
13	$4\text{-}Br\text{-}2,6\text{-}DiCH_3C_6H_2$	105.5	
14	$2,6\text{-}Di\text{-}\underline{i}PrC_6H_3$	99.4	
15	$2\text{-}\underline{i}Pr\text{-}6\text{-}CH_3C_6H_3$	101.2	
16	$4\text{-}CH_3OC_6H_4$	108.5	48.7
17	1-naphthyl	110.8	

a) Reported in ppm; taken at 75°C as 0.5 M solution in dry acetonitrile, with butan-2-one as an internal control.

the nitro group of **1** is 572.2 ppm and is upfield by 2.8 ppm of that of nitrobenzene.[8] This result suggests that the NCO group is a weak electron donor, which is consistent with results noted from ^{13}C nmr studies.[11] The chemical shift range of 14 ppm for the aryl isocyanates is smaller than that noted for ^{17}O chemical shifts of comparably substituted acetophenones (30 ppm)[12] and similar to that for methyl benzoates (15 ppm);[13] however, the latter two systems have the oxygen atom located two bonds from the aryl ring. ^{17}O nmr data for much closer analogs for the isocyanates, systems in which a conjugated double bonded oxygen atom is located three bonds from the aryl ring, are lacking. However, results for two systems have been reported in which the oxygen atom is three bonds from the ring: substituted phenylacetic acids (11 ppm range)[14] and substituted α,N-diaryl nitrones (36 ppm range).[15] The bonding in the three functional groups being compared is vastly different and only an empirical comparison should be made. Nevertheless, it is apparent that substituent effects on the cumulated diene are more comparable in magnitude to the results for the phenylacetic acids than to those for the α,N-diaryl nitrones. Figure 1 illustrates the correlation observed between the ^{17}O chemical shift data for the 4-substituted aryl isocyanates and Hammett σ constants (a poorer correlation was noted with σ^+ constants). The expression for the line with 95% confidence limit error in the slope is $\delta=13.89\ (\pm 1.09)\sigma + 111.7$; $r=0.997$. Due to the rather limited number of 4-substituted compounds, no attempt was made to correlate the data by multi-parameter approaches.

The introduction of substituents ortho to the isocyanate function produces significant shifts depending upon the size of the group (**7**, **8**, **10**, **12-15**). The electronic contributions to the chemical shift are assumed to be the same when a substituent is located at either the ortho or para position relative to the isocyanate group. Consequently, shift differences between ortho and para isomers can be attributed, in large part, to steric effects. The shielding effect of placing an alkyl group ortho to the isocyanate group is consistently greater than is noted when the same alkyl group is placed para to the isocyanate group--compare **6** and **7**--and is attributed to steric influences. Qualitatively, as the size of the alkyl group increases, the magnitude of the upfield shift increases; compare **7**, **10** and **12**. Generally, the addition of a second ortho alkyl group causes further upfield shift; however, the magnitude of the shift is not strictly additive as can be seen by comparing the result for **14** and **15** to those

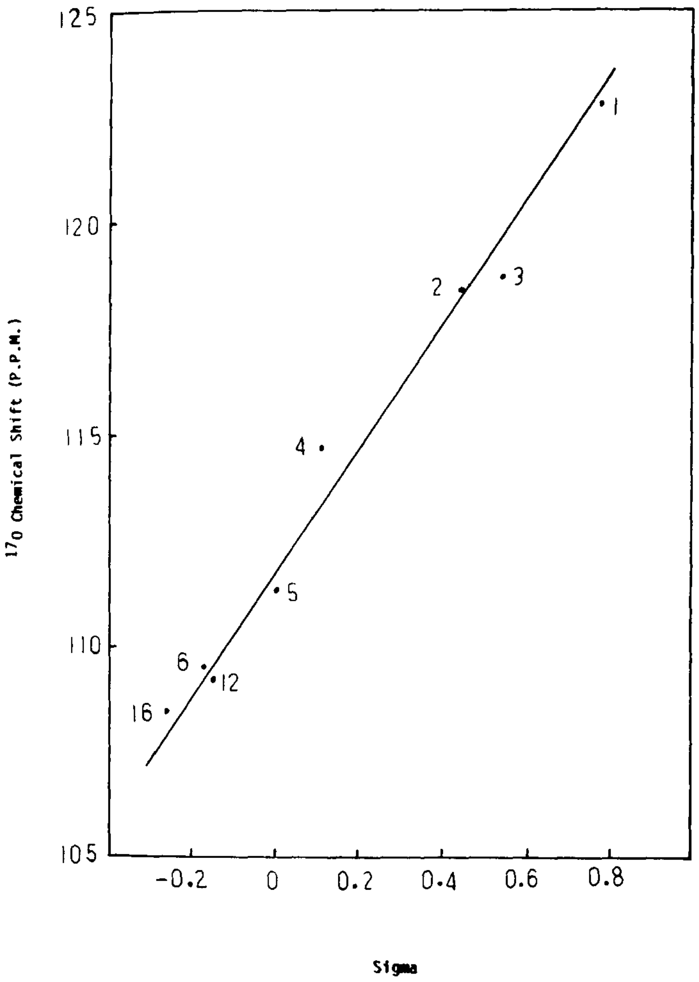

Figure 1. Plot of the ^{17}O chemical shift (ppm) data for 4-substituted phenyl isocyanate *vs.* Hammet sigma constants for the substituents.

of **7** and **12.** The steric influence of a peri hydrogen has been found to cause significant chemical shift changes in a variety of other functional groups;[8,9] in contrast, there is no significant difference between the chemical shift of 1-naphthyl isocyanate **17** and phenyl isocyanate **5.** This result is presumably a consequence of effectively smaller steric requirements of the linear isocyanate group.

The steric influence of the alkyl group on ^{17}O chemical shift of the NCO group, shielding, is in the opposite direction of that noted for a number of similarly substituted functionalities including aldehydes, amides, ketones, carboxylic acids, esters, nitro groups and the NO groups of pyridine N-oxides.[7-10,16,17] These functional groups all experienced downfield chemical shifts on introduction of proximate alkyl groups. These downfield shifts, in systems in which the functional group is free to rotate, were explained in terms of increasing double bond character of the functional group as it rotated out of the plane of the aromatic ring to which it was attached.[8,9] In rigid systems where functional group rotation was not possible, the downfield shift was explained as a consequence of bond angle deformation and repulsive van der Waals interactions.[10] In the case of the ortho substituted aryl isocyanates, attractive van der Waals interactions between the proximate groups may be a partial explanation of the shifts.[18] A better understanding of these upfield shifts must await further studies on the geometry of these systems and examination of the ^{17}O nmr chemical shifts of additional hindered isocyanates.

The isocyanate ^{17}O nmr chemical shift is sensitive to both electronic and steric effects and this method should contribute to a better understanding of the influence of substituents on the structure and reactivity of this functional group.

EXPERIMENTAL

The ^{17}O spectra were recorded on a Varian VXR-400 spectrometer equipped with a 10 mm broad-band probe operated at 54.22

MHz. All spectra were acquired at natural abundance at 75°C in dry acetonitrile (Aldrich) containing 1% of 2-butanone. The concentration of the isocyanates (available from Aldrich or Fairfield) 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, 2 K data points, 90° pulse angle (40 μs pulse width), 300 μs acquisition delay, 29 ms acquisition time and ca. 20,000 scans. 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 8 K data points. The reproducibility of the chemical shift data is estimated to be ±1.0.

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