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^{13}C NMR Spectra of Substituted *o*-Nitroanisoles and *n*-Butyl *o*-Nitrophenyl Ethers

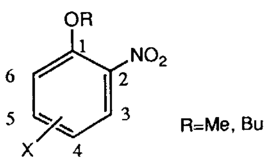
Petrus J. Zeegers* and Malcolm J. Thompson
School of Physical Sciences, Flinders University, Bedford Park, South Australia 5042, Australia

^{13}C NMR analyses of substituted *o*-nitroanisoles and *n*-butyl *o*-nitrophenyl ethers are reported.

KEY WORDS ^{13}C NMR *o*-Nitroanisoles *n*-Butyl *o*-nitrophenyl ethers

INTRODUCTION

As part of a continuing study on the nitration of phenols by the new two-phase procedure,[1,2] some of the *o*-nitrophenol products were methylated with diazomethane or butylated with *n*-bromobutane to give the corresponding *o*-nitroanisole or *n*-butyl *o*-nitrophenyl ethers. These compounds are of spectroscopic interest as the proximity of the two sterically requiring groups makes chemical shift assignment by additive SCS values less certain.[3]



RESULTS

The ^{13}C NMR assignments are summarized in Tables 1 and 2.

DISCUSSION

Using *o*-nitroanisole and *n*-butyl *o*-nitrophenyl ether as the reference compounds (Tables 1 and 2), the effect of the addition of a third substituent was evaluated in terms of the substituent chemical shifts (SCS) of the substituent. Most of the discussion will refer to the *o*-nitroanisoles. For the C-4 and C-5 substituted compounds the reference SCS values[3] for monosubstituted benzenes are a good guide to the value of the SCS values expected on the introduction of the third substituent. The exceptions to this are the methoxy- and the 4-halogeno-substituted compounds. For the latter compounds there is a consistently lower than expected value for the chemical shift of C-2, C-3, C-4 and C-5. For C-1, C-3, C-4 and C-5 the trend is for an increased negative deviation in the SCS on descending the halogen series. The greatest deviation is seen at C-4 for the iodo compound (−7.71 ppm). For C-2 the smallest deviation is seen for the chloro compound (−1.24 ppm) and the largest for the iodo compound (−2.57 ppm), with the trend in the deviation being Cl < Br < F < I. These observed deviations for C-2 are greater than expected for the carbon *meta* to the halogen. For the other *meta* position, C-6, the deviations are considerably smaller and do not show the same trend as for C-2.

The observed trends are consistent for both the *o*-nitroanisoles and the *n*-butyl *o*-nitrophenyl ethers. The other compounds which show a consistent deviation in the SCS are the two compounds with a carbonyl substituent at C-5, *para* to the nitro group.

For the C-3 and C-6 substituted compounds comparison was made with the unsubstituted compound to reveal any differences in the SCS for the carbons *para* to the nitro and the methoxy groups. Deviations in the SCS values for C-4 and C-5 may indicate a steric hindrance of resonance resulting from non-planarity of these two substituent groups. Kitching *et al.*[4] studied the effects of flanking methyl groups on the SCS in a series of 2-X-1,3-dimethylbenzenes. A marked reduction in the expected SCS value at C-4 for the nitro-substituted dimethylbenzene indicated that the nitro group is twisted out of plane, thereby reducing its conjugative electron withdrawal. The preferred conformation of the nitro group to be out of the ring plane was similarly observed when the substituent was methoxy or dimethylamine, each being a substituent with some steric requirement.

All of the 3-substituted *o*-nitroanisoles show a substantial decrease in the expected SCS for C-5. This suggests a reduction of the conjugative electron withdrawal of the nitro group resulting from its non-planar conformation with respect to the ring. A concomitant increase was found for the SCS for C-4, this deviation being largest (2.56 ppm) for the more sterically requiring group (*t*-Bu) and least for the linear CN group (0.98 ppm). These deviations can be accounted for by either an increase in the inductive electron withdrawal or decreased conjugative donation by the methoxy group.

The two positions *ortho* to the nitro group, C-1 and C-3, also show the effect of the non-planarity of the

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* Author to whom correspondence should be addressed.

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Table 1. ^{13}C NMR chemical shifts for substituted *o*-nitroanisoles in ppm downfield from TMS

X	C-1	C-2	C-3	C-4	C-5	C-6	OMe	Substituent
H	152.93	139.66	125.47	120.27	134.41	113.66	56.39	
3-Me	150.77	141.66	130.83	122.60	130.72	110.08	56.31	16.79
3-Et	150.60	141.72	136.77	121.05	130.78	109.96	56.36	24.19, 14.81
3-*t*-Bu	151.17	141.66	141.76	119.73	130.01	110.16	56.53	35.75, 30.77
3-CN	151.98	139.77	106.88	124.85	132.51	117.96	57.01	118.23
4-Me	150.93	139.29	125.74	130.23	134.89	113.60	56.56	20.10
4-Et	151.09	139.44	124.60	136.57	133.76	113.66	56.56	27.57, 15.33
4-*t*-Bu	150.77	139.23	122.27	143.72	131.43	113.44	56.50	34.24, 31.10
4-F	149.82d	139.28d	112.84d	155.21d	121.21d	115.06d	57.10	
	$J^4 = 3$ Hz	$J^3 = 7$ Hz	$J^2 = 27$ Hz	$J^1 = 244$ Hz	$J^2 = 23$ Hz	$J^3 = 7$ Hz		
4-Cl	151.69	139.72	125.47	125.22	134.03	114.90	56.83	
4-Br	152.18	140.04	128.28	111.82	136.95	115.28	56.77	
4-I	152.61	140.04	133.48	80.56	142.75	115.82	56.61	
4-OMe	152.93	139.55	110.08	147.35	120.81	115.23	57.13	56.07
4-CH_2OH	152.23	139.17	124.00	133.43	132.83	113.66	56.61	63.38
4-CHO	157.16	139.93	127.20	129.04	134.89	113.93	57.10	188.85
4-COMe	156.18	139.28	126.00	129.59	134.14	113.44	56.99	194.86, 26.27
4-CN	155.86	139.44	129.42	103.85	137.93	114.96	57.20	116.85
5-Me	153.20	137.27	125.85	120.97	146.16	114.09	56.39	21.94
5-Et	153.35	137.46	126.04	119.76	152.11	112.94	56.43	29.24, 15.28
5-*t*-Bu	153.05	137.28	125.67	117.61	158.99	110.72	56.42	35.58, 31.04
5-OMe	155.72	133.17	128.48	104.79	164.83	99.72	56.49	55.94
5-CHO	152.73	142.32	125.61	120.49	141.06	112.73	56.75	196.22
5-COMe	152.76	142.43	125.62	120.49	141.06	112.72	56.76	196.21, 26.84
6-Me	151.63	144.37	122.76	123.76	135.71	134.57	61.76	15.98
6-t-Bu	153.30	144.30	122.69	123.71	131.32	145.33	61.44	35.66, 30.48
6-OMe	142.91	145.12	116.14	123.72	115.98	154.24	56.47	61.98
3,4-DiMe	148.76	141.50	127.13	129.69	131.38	109.60	56.33	19.20, 14.65
3,5-DiMe	150.77	139.93	130.67	123.14	141.45	110.68	56.18	21.61, 16.96
3,6-DiMe	149.63	146.75	128.18	125.96	132.62	130.45	62.14	16.63, 15.66
4,6-DiMe	149.41	143.94	122.87	133.86	136.41	134.03	61.76	20.48, 15.93
5,6-DiMe	151.58	142.20	122.22	125.20	144.70	132.89	62.03	20.59, 12.40

Table 2. ^{13}C NMR chemical shifts for substituted *n*-butyl *o*-nitrophenyl ethers in ppm downfield from TMS

X	C-1	C-2	C-3	C-4	C-5	C-6	OBu	Substituent
H	152.48	140.04	125.41	120.01	133.99	114.50	69.35, 31.01, 19.10, 13.72	
3-Me	150.39	142.42	130.61	122.33	130.78	111.06	69.13, 30.98, 19.07, 13.71	16.85
4-Me	150.44	139.74	125.58	129.96	134.55	114.59	69.49, 31.09, 19.18, 13.76	20.15
5-Me	152.77	137.60	125.71	120.72	145.64	115.00	69.29, 31.07, 19.13, 13.76	21.91
6-Me	150.82	144.53	122.77	123.45	135.44	134.56	74.49, 32.18, 19.06, 13.87	16.24
4-Et	150.58	139.88	124.46	136.35	133.40	114.54	69.49, 31.09, 19.12, 13.75	27.61 15.33
4-*t*-Bu	150.30	139.61	122.27	143.53	131.01	114.31	69.43, 31.09, 19.12, 13.75	34.30 31.19
4-F	149.13d $J^4 = 3$ Hz	139.51d $J^3 = 6$ Hz	112.57d $J^2 = 27$ Hz	155.08d $J^1 = 243$ Hz	120.88d $J^2 = 23$ Hz	115.97d $J^3 = 7$ Hz	70.10, 31.02, 19.06, 13.67	
4-Cl	151.24	140.03	125.36	124.97	133.80	115.76	69.84, 30.93, 19.07, 13.71	
4-Br	151.70	139.93	128.16	111.51	136.68	116.12	69.79, 30.91, 19.07, 13.85	
4-I	152.36	140.66	133.73	80.27	142.53	116.54	69.66, 30.89, 19.07, 13.74	
4-CH_2OH	151.83	139.72	123.94	133.18	132.53	114.65	69.56, 31.00, 19.09, 137.73	63.64
4,6-DiMe	148.57	144.10	136.23	133.49	134.08	122.87	74.42, 32.17, 19.08, 13.87	20.50, 16.16

nitro group in that they show a substantial negative deviation in the SCS values. The 6-substituted anisoles do not show a consistent change in the SCS for C-5. A pronounced difference was found in the SCS for C-4. The introduction of a substituent has a dramatic effect, with a change in the SCS of 2.45–3.54 ppm. This suggests that the most stable conformer has the nitro group planar with the ring and the C—O—Me plane orthogonal to the ring plane with an associated decrease in its conjugative effect. The 6-OMe compound, with a -4.03 ppm deviation in the SCS for C-5, suggests that in this case the nitro group is also out of plane. The two positions *ortho* to the methoxy group, C-2 and C-6, also exhibit the effect of the non-planarity of the methoxy group in that they show a substantial positive deviation in the SCS. For C-2 the deviation was in the range 4.46–4.77 ppm and for C-6 the deviation was 9.18–11.61 ppm, the most substantial for all the compounds analysed.

NMR SPECTRA

^{13}C NMR spectra were recorded on a JEOL FX 90Q Fourier transform spectrometer or a Varian 300 Gemini Fourier transform spectrometer. Samples were dissolved in deuteriochloroform (*ca.* 0.5 M) using TMS as an internal reference. The deuterium of the solvent was used as a lock signal; 5 mm tubes were used and the probe temperature was 23 °C. Spectra were recorded with complete proton noise decoupling and some spectra were also recorded with proton coupling and with DEPT editing and HETCOR.

The spectral parameters were as follows: JEOL spectrometer, operating frequency 22.533 MHz, sweep width 5000 Hz, pulse width 5.5 μs, pulse delay 2.0 s, flip angle 45°, acquisition time 0.8 s, 8K data points, digital resolution of 1.25 Hz per data, 5000–10 000 transients; Varian spectrometer, operating frequency 75.462 MHz, sweep width 18 762 Hz, pulse width 7.5 μs, pulse delay 2.0 s, flip angle 45°, acquisition time 0.8 s, 30 K data points, digital resolution of 1.25 Hz per data point, 1000–5000 transients.

EXPERIMENTAL

The substituted phenol was nitrated using the two-phase nitration procedure.[1,2] The *o*-nitrophenols were isolated and purified by chromatography on silica gel, eluting with ethyl acetate in hexane. The *o*-nitrophenol was then methylated[5] with an excess of ethereal diazomethane or butylated[6] with *n*-bromobutane in acetone in the presence of K_2CO_3. The alkylated products were isolated and recrystallized from ethanol or distilled under vacuum. The purity of the products was confirmed by gas chromatography–mass spectrometry, accurate mass determination and microanalysis where applicable. Physical data were then compared with literature data.

Most of the *o*-nitroanisoles are known compounds, so only those for which no literature reference could be found are listed here: 4-Et, pale pink oil, b.p. 120 °C/0.05 mmHg; 4-*t*-Bu, yellow oil, b.p. 122 °C/0.02 mmHg; 3-Et, yellow oil, b.p. 120 °C/0.10 mmHg; 5-Et, yellow oil, b.p. 128 °C/0.20 mmHg; 3-*t*-Bu, yellow oil, b.p. 165 °C/0.05 mmHg; 5-*t*-Bu, yellow oil, b.p. 150 °C/0.5 mmHg.

The *n*-butyl *o*-nitrophenyl ethers are new compounds with microanalyses in agreement with the proposed structures: X = H, yellow oil, b.p. 152 °C/0.10 mmHg; 3-Me, yellow oil, b.p. 135 °C/0.20 mmHg; 4-Me, yellow oil, b.p. 190 °C/25 mmHg; 5-Me, yellow oil, b.p. 160 °C/2 mmHg; 6-Me, pale yellow oil, b.p. 115 °C/0.10 mmHg; 4-Et, yellow oil, b.p. 180 °C/20 mmHg; 4-*t*-Bu, pale yellow oil, b.p. 132 °C/0.20 mmHg; 4-F, pale yellow oil, b.p. 165 °C/0.5 mmHg; 4-Cl, pale yellow oil, b.p. 160 °C/0.5 mmHg; 4-Br, pale yellow oil, b.p. 140 °C/0.10 mmHg; 4-I, pale yellow oil, b.p. 150 °C/0.10 mmHg; 4-CH_2OH, pale yellow oil, b.p. 160 °C/0.5 mmHg; 4,6-diMe, yellow oil, b.p. 130 °C/0.10 mmHg.

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