AN ^{17}O NMR SPECTROSCOPY STUDY OF 3-SUBSTITUTED 4-NITROPYRIDINE N-OXIDES

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Abstract: Natural abundance ^{17}O NMR chemical shift data were obtained, in acetonitrile at 75°C, for twelve 3-substituted-4-nitropyridine N-oxides. A plot of the ^{17}O NMR chemical shift data for the nitro group of the nitropyridine N-oxides versus the similar data previously published for *ortho*-substituted nitrobenzenes gave a very good straight line.

Introduction

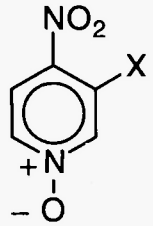
Heteroaromatic N-oxides have been extensively studied due, in part, to the intriguing interplay between the NO group and the heteroaromatic ring.[1,2] The interplay of the two π systems is referred to as a back-donation or push-pull phenomenon.[1,2] The partial π bond order of the NO group depends on substituents and its importance has been assessed in various ways.[1,2] ^{17}O NMR chemical shifts are especially sensitive to the π character of the oxygen of the functional groups and thus ^{17}O NMR spectroscopy has been used to examine the effect of structural changes on back-donation in heterocylic N-oxide systems.[3,4] Recently, we described the effect of *ortho*-substituents on the ^{17}O NMR and IR spectroscopic properties of the nitro group for two series of nitrobenzenes[5] and earlier some of us examined the influence of substituents on the ^{13}C NMR and IR spectroscopic properties of 3-substituted-4-nitropyridine N-oxides .[6,7] Consequently, it seemed of interest to study the influence of 3-substituents on 4-nitropyridine N-oxides by ^{17}O NMR spectroscopic methods in order to examine both the direct effect on the nitro group and the indirect steric effect on the back-donation process.

Results and Discussion

The ^{17}O NMR chemical shift data, obtained at natural abundance in dry acetonitrile at 75°C, for the pyridine N-oxides are listed in Table 1. The ^{17}O NMR chemical shift values for the NO_2 group for the compounds ranges from 601.1 ppm for **1** to 557.0 ppm for **12**.

The ^{17}O NMR chemical shifts of the NO_2 groups for **1- 8** are upfield by approximately 10 ppm of those for the corresponding *ortho*-substituted nitrobenzenes[5] , the data for the

Table 1. ^{17}O NMR and IR Spectroscopy Data for 3-Substituted-4-Nitro pyridine-N-oxides.



Compd. No.	X	δ (NO_2) [a]	δ (NO) [b]	νs(NO_2)[c]	ν (NO)[c]
1	Cl	601.1	418.9	1343.6	1240.8
2	Br	599.7	417.6	1344.0	1241.6
3	CH_2CH_3	596.7	406.0	1344.0	1236.0
4	F	595.9	434.6	1350.4	1235.2
5	[d]$COOCH_3$	594.9	419.1	1351.8	1251.2
6	$N(CH_3)_2$	594.0	397.5	1332.8	1240.0
7	CH_3	593.2	405.2	1344.0	1258.0
8	I	593.0	413.8	1340.4	1243.2
9	H	575.2	418.7	1342.0	
10	NH_2	563.8	404.0	1329.2	1250.4
11	$NHCH_3$	559.0	415.5	1353.6	1241.6
12	NHtBu	557.0	412.8	1345.6	1244.0

a) The details of the instrument operation conditions for ^{17}O NMR data collection may be found in ref. 5. ^{17}O NMR chemical shifts, in ppm, were determined in acetonitrile at 75°C. The half-width at peak half-height for all nitro signals are 510±100 Hz. b) ^{17}O NMR chemical values for the NO signals shifts are in ppm; the half-width at peak half-height for the NO signal are 630 Hz ±140, except for **8** which is 850 Hz. c) IR stretching frequencies in cm^{-1}; determined in chloroform at room temperature as described in ref. 7. d) The signals for the $COOCH_3$ group are 370.0δ(470 Hz) and 145.2δ(400Hz).

remaining compounds **9-12** are within 1-2 ppm of that of the *ortho*-substituted nitrobenzene counterparts. The observed upfield shifts are consistent with back-donation from the NO group. The IR spectroscopy data , obtained in chloroform solution, for the symmetric stretching vibrations of the NO_2 group of the pyridine-N-oxides have been previously reported by some of us[6,7], with the exception of compound **12**, are also listed in Table 1. Table 1 contains the symmetric stretching values of the NO_2 group along with the previously unreported values for the NO stretch. The compounds exhibit the typical

absorption bands in the region 1329-1350 cm^{-1} arising from the symmetric stretching vibrations of the NO_2 group. This range is shifted towards higher wave numbers in comparison with the absorption range of similar *ortho*-substituted nitrobenzenes[11] and is consistent with back-donation from the NO group.

On plotting the NO_2 group ^{17}O NMR chemical shift data for the pyridine-N-oxides versus analogous data for *ortho*-substituted nitrobenzenes[5] a good straight line is obtained; the expression for the line is: $\delta(NO2)p = 0.74\delta(NO_2)b + 146.9$, $r^2 = 0.985$. The good correlation between the two sets of data suggest that factors influencing both systems are similar. The slope of the line indicates that pyridine-N-oxides are less sensitive to substituent effects by approximately 26% when compared to *ortho*-substituted nitrobenzenes. The diminution in substitutent effects can be attributed to the resistance to rotation of the nitro group of the pyridine-N-oxide as a consequence of conjugation with the NO group via back-donation.

IR stretching frequency and ^{17}O NMR chemical shift correlations for several functional groups have been reported and the correlations linked to the bond order electron density matrix of the Karplus-Pople expression.[8-10] Consequently, it is of interest to plot the nitro group ^{17}O NMR chemical shift values versus IR stretching frequency values for the nitro group of the pyridine-N-oxides. We found previously that similar plots for the *ortho*-substituted nitrobenzene series yielded graphs which were interpreted as consisting of two lines, one line representing the non-hydrogen bonding compounds and a second one representing the R-N-H hydrogen bonding ones. In this study we have fewer data points and consequently analysis of the plot (not shown) must be pursed with caution . The three points for substituents capable of intramoleular hydrogen bonding for the pyridine-N-oxide system are clustered away from the remaining points, suggesting that hydrogen bonding is also important in the 3-substituted-4-nitropyridine N-oxide system, as noted for two nitrobenzene series.[5] This conclusion is in direct contrast to conclusions drawn from ^{13}C NMR spectroscopic studies on this same pyridine-N-oxide system.[11] Intrinsically, there does not seem a reason to expect the absence of intramoleular hydrogen bonding in this system. The different conclusions drawn from the ^{13}C NMR and the ^{17}O NMR studies may be a result of the greater sensitivity of ^{17}O NMR chemical shifts to hydrogen bonding effects . [12,13]

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References

(1) A. R. Katritzky and J. M. Lagowski, *Chemistry of Heterocyclic N-oxides*, Academic Press, London, (1971)

(2) E. Ochiai, *Aromatic Amine Oxides*, Elsevier, New York, (1967)

(3) D.W. Boykin, A. L. Baumstark and P. Balakrishnan, Mag. Reson. Chem. 23, 276 (1985)

(4) D.W. Boykin, P. Balakrishnan and A. L. Baumstark, Mag. Reson. Chem. 23, 695 (1985)

(5) A. Perjéssy, D. Rasala, R. Gawinecki, and D. W. Boykin, J. Mol. Structure 382 , 93 (1996)

(6) D. Rasala and R. Gawinecki, Bull. Soc. Chim. Fr., 128 , 201 (1991)

(7) A. Perjéssy, D. Rasala, and R. Gawinecki, Polish J. Chem, 69, 1659 (1995)

(8) D. W. Boykin, A. L. Baumstark, P. Balakrishnan, A. Perjéssy, and P. Hrnciar, Spectrochimica Acta, 40A. 887 (1984)

(9) M. Karplus and J. A. Pople, J. Chem. Phys., 38 , 2803 (1963)

(10) J.-P. Kintzinger, in: P. Diehl, E. Fluck, R. Kosfield (Eds), NMR-17, *Oxygen-17 and Silicon-29*, Springer-Verlag, Berlin, pp 1-64 (1981)

(11) D. Rasala, R. Gawinecki, , W. Kraus and P. Tomasik, Chem. Scripta, 25 , 345 (1985)

(12) D.W. Boykin, ed., "^{17}O NMR Spectroscopy in Organic Chemistry," CRC Press, Boca Raton, FL, (1991)

(13) D.W. Boykin, "Applications of ^{17}O NMR Spectroscopy to Natural Products Chemistry," in *Studies in Natural Products Chemistry*, Vol. 17., Atur-ur Rahman, ed., Elsevier, Amsterdam, (1995) pp. 549-600.

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