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^{17}O Nuclear Magnetic Resonance Studies. V.[1] ^{17}O Shieldings of Some Substituted Anisoles

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Synopsis. Fourier transform ^{17}O NMR spectra have been measured for a number of meta and para substituted anisoles in natural abundance at 10.8 MHz. The shielding of the methoxyl oxygen nucleus decreases as the electron-withdrawing substituents are introduced to the ring. A good linear correlation is obtained for a plot of the ^{17}O shifts *versus* the Hammett σ^- constants.

Proton nuclear magnetic resonance studies have shown that methoxyl proton shifts are linearly related to the Hammett σ parameter.[2] A similar but only a slight dependence of methoxyl ^{13}C shifts on the nuclear substitution has been reported.[3] In order to investigate the effects of nuclear substitution on the methoxyl oxygen shielding, we have now measured the ^{17}O NMR shifts of a series of sixteen anisoles.

It is apparent from the observed data collected in Table 1 that the oxygen shifts are highly sensitive to meta and para substitution on the ring; they cover a rather wide total range of 30 ppm. It is easily expected that electron-withdrawing groups on the ring decrease the shielding at the oxygen nucleus, since the conjugative electron release from the oxygen will be enhanced. This general trend is exactly what was observed for the ^{17}O chemical shifts of anisoles. A plot of the methoxyl oxygen shifts *versus* the Hammett σ^- values reveals a good linear correlation between the two parameters ($\rho=16.2$ ppm, correlation coefficient r of 0.963). Analyses of the data according to the Yukawa-Tsuno equation, $\Delta\delta=\rho\{\sigma^\circ+\gamma(\sigma^- - \sigma^\circ)\}$, give the following values: $\rho=17.2$ ppm and $\gamma=0.881$.[4] A quantitative measure of the resonance interaction of the methoxyl group with para substituents is thus obtained. These results may be compared with the Hammett σ dependence of the methoxyl hydrogen ($\rho=0.24$ ppm)[2] and carbon chemical shifts.[3]

Table 1. ^{17}O NMR shifts of p- and m-substituted anisoles

Substituent	δ^{17}O/ppm	π-Bond order $\times 10^2$	π-Electron density
p-NH$_2$	139[a]	4.03	1.905
p-OCH$_3$	141	4.16	1.902
p-C(CH$_3$)$_3$	147		
p-CH$_3$	147	4.32	1.899
p-F	148	4.27	1.900
H	151	4.36	1.898
p-Cl	151		
p-Br	154		
p-CF$_3$	157		
p-CN	163	4.49	1.894
p-NO$_2$	170	4.72	1.888
m-NH$_2$	149		
m-Cl	154		
m-Br	155		
m-F	156		
m-NO$_2$	166		

a) Subtract 103 ppm from the shift values to convert them into the data referenced to external H$_2$O.

Theoretical reasoning of the shielding pattern observed here is not so easy as it would be understood intuitively. The diamagnetic electric current about the nucleus which is directly affected by polar substituents play a major role in governing the chemical shifts of ^{1}H NMR, but not of ^{13}C and ^{17}O nuclei. The paramagnetic screening is considered to dominate the chemical shifts of the latter nuclei. Decrease of shielding with the increasing electron-withdrawal should be explained by increase in the mean inverse cube of the 2p electron radius $\langle r^{-3}\rangle_{\mathrm{oxygen}}$ and/or in the orbital terms $[Q_{\mathrm{AA}}+\Sigma Q_{\mathrm{AB}}]$ in the Karplus-Pople expression of the paramagnetic screening (Eq. 1).[5]

$$\sigma_{\mathrm{p}}^{\mathrm{A}} = -\frac{e^2\hbar^2\langle r^{-3}\rangle}{2m^2c^2(\Delta E)}[Q_{\mathrm{AA}}+\sum_{\mathrm{A}\neq\mathrm{B}}(Q_{\mathrm{AB}})] \qquad (1)$$

Decreasing charge density at the oxygen is expected to lead to a contraction of the 2p orbitals and thereby an increase in the paramagnetic screening. The good linear correlations were obtained between the observed ^{17}O chemical shifts on the one hand and the π-electron densities at the oxygen (2040 ppm/π-electron, $r=0.993$) or the π-bond orders between the oxygen and the aromatic carbon attached to it (4770 ppm/π-bond order, $r=0.974$) calculated by the CNDO/2 methods on the other.[6]

The trend observed here for the anisoles is just the opposite to that of the oxygen nuclei of the aliphatic ethers in which the more electron-donating tertiary alkyl ethers are deshielded compared to less electron-donating primary alkyl ethers.[7] Whereas the change in the effective excitation energy ΔE in Eq. 1 was a dominant factor in the paramagnetic screening there,[7] both the n- and π^*-levels would be affected simultaneously by the ring substituents in the anisoles, leaving the effect of ΔE term less obvious.

We conclude that one of the most direct experimental evidence for the dependence of the electron density about the methoxyl oxygen nucleus on the ring substituents was obtained by the ^{17}O NMR shifts.

Experimental

Pulsed Fourier transform spectra were obtained on a Varian FT-80A spectrometer at 10.8 MHz. A pulse width of 35 μs with an acquisition time of 0.02 s was employed with a spectral width of 8000 Hz. Anywhere between 3×10^6 and 4×10^7 transients were accumulated depending on the sample. Chemical shifts were read as frequency shifts from the synthesizer setting (8.53200 MHz), expressed in ppm, and judged to be accurate to ±1 ppm (the Fourier number was at 1,6384). The spectra were run at 80 °C on pure, natural-abundance samples (1.0—1.4 g) dissolved in chloroform-*d* (0.9—1.2 ml) which also provided an internal deuterium lock signal.

p-*t*-Butyl- and *m*-chloroanisoles were prepared from the corresponding phenols by the standard methylation with dimethyl sulfate. The others were commercial samples of reliable grade and were used directly.

The π-electron densities and π-bond orders were calculated by the CNDO/2 methods with the aid of the program No. 141 of QCPE on a HITAC M-180 system of this institute. Molecular geometries employed for the framework of anisoles were basically those reported for 4,4′-anisoin[8] and the standard bond lengths and angles[6] were used otherwise.

References

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