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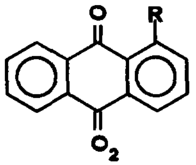
^{17}O NMR Spectroscopy: Origin of Deshielding Effects in Rigid, Planar Molecules

A.L. Baumstark,* M. Dotrong, R.R. Stark and D.W. Boykin*

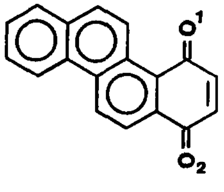
Department of Chemistry and LMBS, Georgia State University, Atlanta, Georgia 30303-3083 USA

Summary: ^{17}O NMR data for hindered carbonyls in planar quinones and flavones showed large deshielding effects and correlated with estimated repulsive van der Waals interactions, providing new insights into steric phenomenon at carbonyl oxygens.

^{17}O NMR spectroscopy has developed into an important method for examining a wide variety of structural problems[1] and should provide new insights into the understanding of chemical reactivity.[2] Quantitative relationships have been demonstrated for ^{17}O NMR data and torsion angles for a variety of aromatic carbonyl[3-5] and nitro[6] compounds. ^{17}O NMR studies on rigid, planar aromatic systems have shown unexpected sensitivity to non-torsional structural variations.[2,7] ^{17}O NMR data for series of hindered phthalic anhydrides,[2] phthalides,[7] and phthalimides[7] paralleled in-plane structural distortions; deshielding effects were observed for carbonyl groups with distorted bond angles.[2,7] These ^{17}O data provided new information since in marked contrast, the ^{13}C NMR data for hindered carbonyl groups were not sensitive to structural changes.[2,7] We report ^{17}O NMR data for a series of quinones (**1-9**) and flavones (**10-12**) which reflect non-torsional structural effects and a general correlation of relative ^{17}O chemical shifts for a number of different structural types with estimated repulsive van der Waals interactions.



3 R = CH_3
5 R = t-Bu



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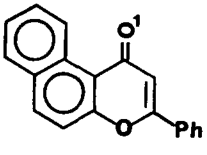

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The ^{17}O NMR data of a series of anthraquinones **1-7**, naphthoquinone **8**, 1,4-chrysenequinone **9**, and several flavones **10-12** in acetonitrile at 75°C are shown in Table 1. In compounds which contain hindered and unhindered carbonyl groups, two well-separated signals are observed. Spectra for the 2- and 1-methylanthraquinones (**2**, **3**) are shown in Figure 1. The data for **2** show the small shielding effects expected based upon electronic interactions of the methyl group.[8] Of the two signals observed for **3**, one is found to be slightly shielded as expected. However, the other signal for **3** is deshielded by 28 ppm and is assigned to the hindered carbonyl ortho to the methyl group. This downfield shift for **3** is larger than that noted for analogous phthalide and phthalimide systems.[2,7] The signal for the hindered carbonyl of 1-*t*-butylanthraquinone **5** is even further downfield (50 ppm) despite the fact that the electronic effects are essentially constant. In contrast, essentially no effect is noted for 1-phenyl substitution (**7**). In the chyrsene compound **9** the carbonyl adjacent to a *peri* type hydrogen is deshielded whereas the signal for the unhindered carbonyl group is essentially the same as in the parent naphthoquinone. Consistent with these observations, the hindered carbonyl of the flavone **12** shows substantial deshielding effects in contrast to that of the unhindered isomer **11** which shows a modest shielding effect compared to the results for the parent **10**. It is clear that the deshielded signals arise from the hindered carbonyls and the 50 ppm downfield shift for **5** is the largest steric induced shift observed to date.

Table I. ^{17}O Chemical Shift Data[a] for (^{17}O-Enriched) Substituted Anthraquinones and Flavones in CH_3CN at 75°C.

No.	Compound	$\delta(C{=}O)_1$[b]	$\delta(C{=}O)_2$	No.	Compound	$\delta(C{=}O)_1$[b]	$\delta(C{=}O)_2$
1	anthraquinone	524	524	**7**[c]	1-phenylanthraquinone	524[c]	524[c]
2	2-methylanthraquinone	524	519	**8**	naphthoquinone	572	572
3	1-methylanthraquinone	552	521	**9**	1,4-chrysenequinone	602	575
4[c]	2-*t*-butylanthraquinone	523[c]	523[c]	**10**	flavone[d]	--	438
5	1-*t*-butylanthraquinone	572	522	**11**	7,8-benzoflavone	--	433
6[c]	2-phenylanthraquinone	525[c]	525[c]	**12**	5,6-benzoflavone	451	--

a) ±1 ppm. b) The hindered carbonyl group. c) At natural abundance, a broad (500-650 Hz) unresolved signal was observed. d) -O- at 158 ppm.

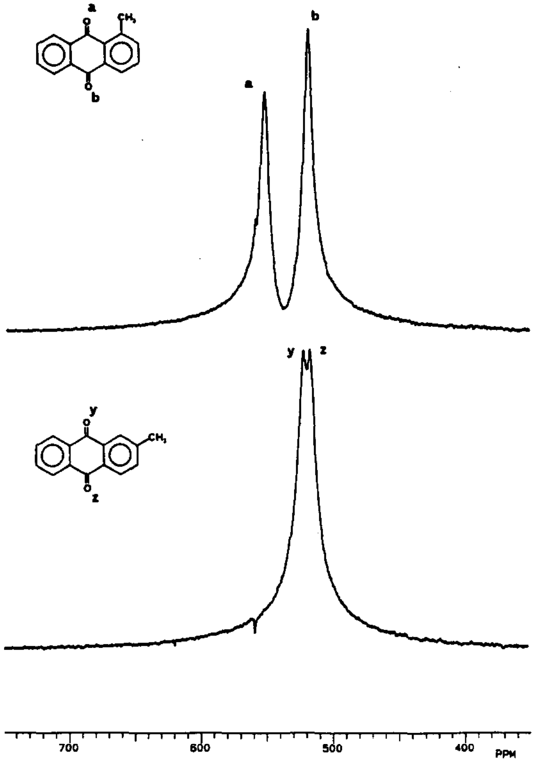

Figure 1. ^{17}O NMR spectra for 1- and 2-methylanthraquinone.

^{17}O spectra, obtained on a Varian VXR-400 spectrometer equipped with a 10 mm broad-band probe, were acquired at 75°C in acetonitrile (Aldrich, anhydrous gold label under nitrogen) containing 1% of 2-butanone (558±1 ppm) as an internal standard. The carbonyl compounds employed in these experiments were enriched with ^{17}O by the previously reported method.[9] The signals were referenced to external deionized water at 75°C. The instrumental settings were, at 54.22 MHz, spectral width 35 kMz, 2 K data points, 90° pulse angle (23 μs pulse width), 300 μs acquisition delay, 29 ms acquisition time and ca. 10,000 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.

Molecular mechanics[5,10] calculations predicted that all compounds in this series were planar. In-plane bond angle distortions were noted for the hindered carbonyl group in each case. For example, in the system which showed the largest deshielded signal, **5**, the hindered carbonyl was predicted to show a bond angle of 125°. To confirm the molecular mechanics calculations, an X-ray structure for the most hindered compound **5** was obtained. The results from the X-ray analysis were in excellent agreement with the MM2 predictions; the hindered carbonyl bond angle was 125° and the anthraquinone ring system was planar.[10c] It is thus clear that torsion angle changes are not the origin of the large deshielding effects observed.

^{17}O chemical shifts are generally described[1] by the paramagnetic term of the Karplus-Pople equation.[11] Chesnut has shown that repulsive van der Waals interactions could explain deshielding trends for ^{13}C and ^{31}P data and suggested this explanation is general to other resonant nuclei.[12] A correlation between local steric energies and ^{13}C NMR data was demonstrated for aliphatic systems.[12] It was suggested that orbital size contraction influenced the paramagnetic screening constant to yield a net deshielding shift. Qualitatively, deshielding effects on ^{17}O chemical shift data in hindered rigid systems seem consistent with this explanation.[2,7]

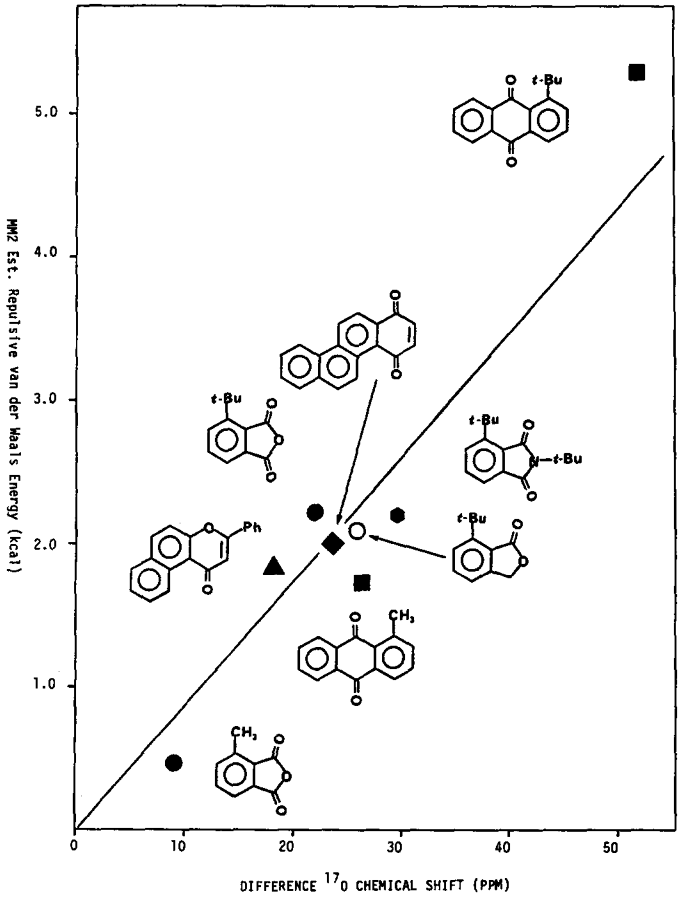

Figure 2. Correlation of est. van der Waals repulsive interactions vs ^{17}O chemical shift difference values.

The relationship of repulsive van der Waals interaction to ^{17}O chemical shift data have not been quantitated. Repulsive van der Waals interactions between the substituent and the carbonyl were estimated by comparing the total MM2 calculated van der Waals energies of a hindered isomer to that of a non-hindered one. The compounds that showed the most distorted bond angles also showed larger values for repulsive van der Waals energies. A plot of the estimated repulsive van der Waals energy versus ^{17}O chemical shift difference values (δ hindered carbonyl-δ parent carbonyl) for many structural types, which represent the net deshielding effect on the hindered carbonyl, is shown in Figure 2.[13] This plot indicates a reasonable correlation for a wide variety of structural types especially keeping in mind that the method of estimation of repulsive van der Waals energies is probably only valid to ±1 kcal. These results show that the bond angle distortions accommodated in these molecules did not allow for the complete elimination of repulsive van der Waals interactions and demonstrate an apparent linear correlation between the net ^{17}O chemical shift and repulsive van der Waals interactions. Thus, consistent with the conclusions of Chesnut, these results show that an origin of the downfield chemical shifts in rigid planar systems is repulsive van der Waals interactions. This methodology provides a new approach for evaluation and understanding of steric phenomenon at carbonyl oxygens in rigid systems.

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13. The datum for the parent compound of each series would appear at the origin in Figure 2.

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