NMR of Terminal Oxygen. Part 11.[†] ^{17}O NMR Spectra of Disilyl ketone and Related Compounds: A Case of Strong Deshielding by Electronic Excitation Energy

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The important deshielding effect on the ^{17}O signal of the disilyl ketone **1** ($\Delta\delta$ *ca.* 400 ppm, compared with normal ketones such as **3**) and of the monosilylketones **2**, is proportional to the λ values of the UV–VIS absorption spectra; in agreement with the r-term of the Karplus–Pople eqn. (1), it is four times larger than the analogous effect on the ^{13}C signals of the carbonyl carbon.

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^{17}O NMR shift values have been found useful to classify the electrophilicity (bond order) of carbonyl compounds;[1] this is in contrast to ^{13}C NMR shift data, which are often the result of compensating factors, not all of which are well understood. When the carbonyl of $-COX$ is bound to an electron-donating second-row element ($X = NR_2$, OR, F), the resulting bond resonance diminishes the π-bond order, increases the electron density around O and increases the ^{17}O NMR shielding. For instance in the absence of resonance (X = Me), PhCOMe shows $\delta_O = 549$, whereas for the resonance-stabilized carbonyl groups in $PhCO_2Me$ $\delta_O = 337$, $PhCONH_2$ $\delta_O = 326$ and $PhCO_2^-$ $\delta_O = 265$.[2]

In special cases, however, influences other than bond order have to be considered for the δ_O values of carbonyl compounds.[3] The chemical shifts of nuclei higher than H are approximated by the Karplus–Pople eqn. (1),[4] where σ^p represents the

$$\sigma^p = -\text{const.} \times \Delta E^{-1} \times r^{-3} \times \Sigma Q \qquad (1)$$

(paramagnetic) shielding; ΔE is the electronic excitation energy, empirically approximated by the longest-wave (symmetry-forbidden) absorption in the UV–VIS spectrum, r is the radius of the p orbital around the atom measured, and ΣQ the charge density–bond order matrix, approximated by the π-bond order at the measured atom. Eqn. (1) shows why molecules with π-bonds are particularly deshielded, in ^{13}C as in ^{17}O NMR.

For carbonyl groups, deshielding influences, *via* ΔE, become important when CO is conjugated with a third-row (or higher) element, particularly X = Si or P: from the colourless di-*tert*-butyl ketone $Me_3CCOCMe_3$ **3**, to the yellow pivaloylsilane $Me_3CCOSiMe_3$ **2**, the magnetically active, symmetry-forbidden UV band (type $n \longrightarrow \pi^*$) passes from 298 to 367 nm;[5] in the red bis(trimethylsilyl) ketone $Me_3SiCOSiMe_3$ **1**[6] the red-shift in the UV–VIS spectrum is particularly strong: $\lambda_{max} = 533$ nm; it has been analysed by different experimental methods and by calculation.[6] The reduction of the excitation energy is due to an important destabilization of the HOMO and a simultaneous lesser stabilization of the LUMO.[5,7] At the same time the ^{13}C shift values rise from 218 for **3** to 249 for **2** to 318 ppm for **1**. Barbarella and Bongini[8] have demonstrated that this low-field shift of the ^{13}C signals is essentially due to changes in the ΔE term[10] and not to changes in the bond order–charge density term.[9] As ^{17}O shift values provide a much better indicator of the bonding state of the carbonyl group than ^{13}C, we have measured (or remeasured) δ_O for **1**, **2**, and **3**, in order to establish whether a correlation between λ_{max} and δ_O exists.

Table 1 ^{17}O and ^{13}C NMR chemical shift values and UV–VIS absorptions ($n \longrightarrow \pi^*$) of trimethylsilyl ketones

Compound	δ_O[a]	δ_C[b]	λ/nm
$Me_3Si-CO-SiMe_3$ **1**	956.4[c]	318.2[9]	533[6]
$Me_3Si-CO-CMe_3$ **2**	666.5[c]	249.0[9]	367[8]
$Me_3Si-CO-Ph$	681[12]	236.7[10]	424[5]
$Me_3C-CO-CMe_3$ **3**	555.2[c]	218.0[8]	298[8]
$Me_3C-CO-Ph$	563[3]	209.1[9]	320[5]

[a] Chemical shifts were measured at natural abundance in *ca.* 0.5 mol dm^{-3} acetonitrile solution at 40 °C, on a Bruker WH 360 spectrometer operating at 48.8 MHz; $\delta_O(H_2O) = 0.0$; for spectral acquisition parameters see Ref. 3. [b] In $CHCl_3$ or $CDCl_3$. [c] This work.

As the results show (Table 1), the δ_O value of **3** is found at 555 ppm, close to that of other acyclic ketones, *e.g.* acetone 571 ppm.[2] The acylsilane **2** shows $\delta_O = 666$,[11] similar to the values of p-$XC_6H_4COSiMe_3$ (632 to 706 ppm, depending upon X; for X = H: $\delta_O = 681$[12]); the deshielding $\Delta\delta_O$ is *ca.* 110 ppm. The disilylketone **1** is still much more deshielded: $\delta_O = 956$, *i.e.* 400 ppm downfield from ordinary ketones R_2CO. This is by far the most deshielded of all C-bound oxygen atoms measured until now. The shift difference from **2** to **1**, nearly 300 ppm, much larger than that from **3** to **2**, corresponds to the red-shift in the UV–VIS spectra: a plot of δ_O over λ is linear, with a slope 1.63 of the correlation line. Applying eqn. (1), one can estimate that the ΔE term alone would induce *ca.* 550 ppm deshielding of **1** compared with **3**. This is slightly more than the 401 ppm found, but close enough to identify ΔE as the preponderant term for these compounds; the difference might be attributed to compensating influences of the other terms of eqn. (1), which are neglected in our crude estimation.

For the ^{13}C signals of **1**, **2** and **3** Barbarella and Bongini[8] had found a linear correlation of δ_C with λ, with a slope 0.41, much smaller than the value of 1.63 found for δ_O/λ; *i.e.* δ_C is much less sensitive to variations of structure than δ_O. The same is true if one compares the benzoyl compounds $PhCOSiMe_3$ and $PhCOCMe_3$ (Table 1): in ^{17}O the shift difference is 118 ppm, in ^{13}C only 27 ppm.

For compounds **1**, **2** and **3**, the ratio of the δ/λ slopes of ^{17}O and ^{13}C, which is the slope δ_O/δ_C of a correlation line of δ_O with δ_C, is 4.0. This is a significant figure: eqn. (1) is applicable to ^{13}C

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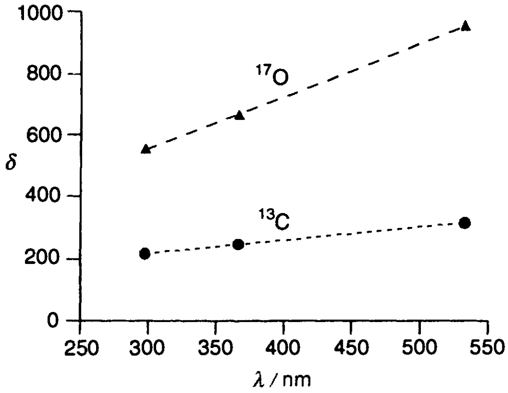

Fig. 1 Plot of the ^{17}O and ^{13}C shift values of ketones **1**, **2** and **3** *vs.* λ_{max} of the n ⟶ π* absorption band

as to ^{17}O NMR; for δ_O and δ_C of the same compound, the ΔE-term must be identical; furthermore, changes in the bond-order term ΣQ might be negligible, at least in a first approximation. Then δ_O/δ_C represents $(r_O^{-3})/(r_C^{-3})$ derived from eqn. (1), that is the ratio of the mean inverse cubes of the radii of the 2p orbitals on O and C respectively.[13] The result of 4.0 is in reasonable agreement with the expected value for $(r_O^{-3})/(r_C^{-3}) = 3.5$, taken from optical spectroscopy.[14] In the case of δ_C values MNDO calculations of **1**, **2** and **3** had supported the preponderance of the ΔE term;[8] as δ_O and δ_C are firmly correlated, the electronic excitation term must be predominant for δ_O too.

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