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DIFFERENTIATION BETWEEN ALPHA AND BETA CARBONS IN ASYMMETRICALLY ORTHO-DISUBSTITUTED AROMATIC MOLECULES BY CARBON-13 NMR SPECTROSCOPY

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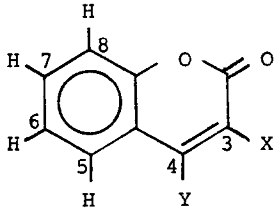
A recent paper[2] has described the use of the fingerprint patterns produced in $^{13}C-\{^1H\}$ decoupled spectra in order to distinguish between the α and β carbons in such symmetrical systems as indan and a cyclohexadiene derivative. The assignments for these fingerprint signals were confirmed by simulation of the off-resonance single-frequency decoupled spectra.

In the course of an extensive study of the ^{13}C chemical shifts and $^{13}C-^1H$ coupling constants in a wide range of coumarin derivatives[3] we have made use of off-resonance single-frequency decoupling experiments as an aid to signal assignments, and wish to report that the "fingerprint" identification of the two α and two β carbons in the unsymmetrical ortho-disubstituted benzenoid ring of a series of 3- and 4-substituted coumarins (I) may readily be achieved.

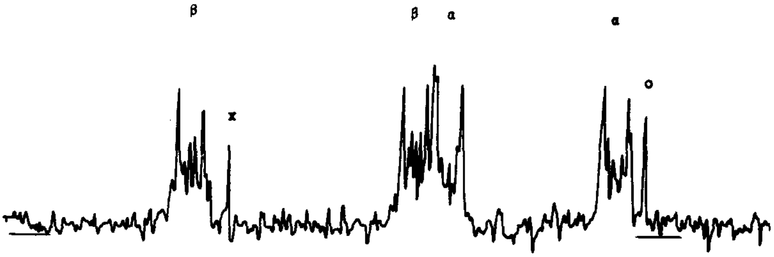


I a - f

a. X = Y = H
b. X = CH_3 Y = H
c. X = OH Y = H
d. X = H Y = CH_3
e. X = H Y = OH
f. X = H Y = OCH_3

In these systems four benzenoid carbon signals are expected, two of which (C_5 and C_8) may be considered as "alpha" carbons, the others (C_6 and C_7) being "beta".

The best position for the off-resonance decoupling frequency, ν_2, is found by trial and error. This is not time-consuming or tedious, and the placement will depend on the separation between the chemically shifted carbon signals. Even when signals are quite strongly overlapped it is possible to recognise the patterns for α and β resonances quite readily. An example, obtained using a Varian CFT-20 spectrometer, is shown in the Figure. The spectrum (from 4-methoxy coumarin) illustrates the shapes well. The α signals are characterised by a sharp flanking pair of lines with relatively smooth outer profiles, and a fairly deep central trough which contains some weak transitions. With the β signals,



FIGURE

The line marked o arises from a quaternary carbon.

(The x denotes a noise spike.)

the central trough is less pronounced, and contains stronger transitions than with the α resonances. The outer strong lines normally show further weak transitions on their outer flanks. Even when signals are very close and therefore become strongly overlapped, it is still possible to recognise these patterns without difficulty. By superimposing isolated α or β multiplets on the envelope from an overlapped αβ pair it is possible to account for all lines in the total signal.

We therefore suggest that this procedure may easily be utilised in ^{13}C NMR spectroscopy to demonstrate the presence of any ortho-disubstituted aromatic (or similar) structural unit, whether or not the grouping is in a symmetrical environment, providing that signals are not completely overlapped.

References

[1] To whom all correspondence should be addressed.
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[3] N. J. Cussans and T. N. Huckerby, papers submitted for publication in Tetrahedron.