Chemistry of the Phenoxathiins VI. An Examination of the ^{13}C-^{1}H Coupling Constants of 1-Azaphenoxathiin by Selective Excitation Fourier Transform ^{13}C-NMR

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The complete examination of coupled ^{13}C-nmr spectra of complex heterocyclic systems is seldom attempted because of the inherrent complexity of these spectra, arising through extensive spin-multiplet overlapping. The utilization of the selective excitation technique, in combination with gated decoupling for the specific re-examination of the primary coupling constants of resonances at the 4- and 6-positions of the 1-azaphenoxathiin ring system is described.

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Sir:

We have recently described the synthesis of the parent 1-azaphenoxathiin ring system (1) as well as a variety of substituted analogs (2-4). Comparison of the primary, one bond coupling constants ($^{1}J_{CH}$) for the 4- and 6-positions of the parent 1-azaphenoxathiin ring system with the corresponding resonances of the substituted systems showed substantial disparity. In all cases, the substituted analogs were observed to possess coupling constants consistent with those normally observed in simple aromatic systems (5). This is in contrast to the originally reported coupling constants, $^{1}J_{C_4H_4}$ = 184.1 Hz and $^{1}J_{C_6H_6}$ = 182.2 Hz in the case of the parent ring system (1). On this basis, the spin-multiplets of the C-4 and C-6 resonances have been examined by the selective excitation procedure of Bodenhausen, Freeman and Morris (6) under gated decoupling conditions (7).

The complex nature of gated decoupled ^{13}C-nmr spectra has largely discouraged many workers from their complete analysis, despite the useful information they invariably contain. This complexity is a direct result of the relative magnitude of the primary ^{13}C-^{1}H coupling constants. Thus, in systems such as heteroaromatics, where there may be large numbers of carbon atoms with substantially similar chemical shifts, extensive spin-multiplet overlapping is common. Such indeed is the case with the gated decoupled spectrum of 1-azaphenoxathiin (1), which is severely overlapped, although not degenerately. Selective excitation ^{13}C-nmr spectroscopy was applied specifically to the C-4 and C-6 resonances to allow the discrete and unequivocal measurement of the coupling constants associated with these resonances, as is shown in Figure 1.

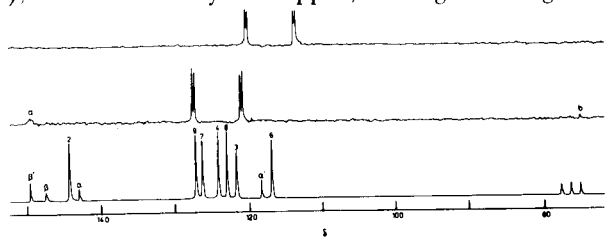


Figure 1. 25.158 MHz ^{13}C-nmr spectrum of 1-azaphenoxathiin (bottom); selective excitation with gated decoupling C-4 resonance; a = β' resonance excited by second harmonic, b = upfield resonance of deuteriochloroform multiplet harmonically excited (middle); selective excitation with gated decoupling C-6 resonance (top).

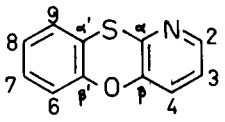
Selective excitation, as developed by Bodenhausen, Freeman and Morris (6) relys on a series of attenuated pulses (8) applied at precisely spaced intervals in a manner very much analogous to the familiar T_2-Carr Purcell sequence (9). The pulse interval is defined by the rate of precession occurring following a pulse, governed by $\theta = 2\pi\tau\Delta f$. Relative to the carrier frequency of the spectrometer, this condition may also be expressed as $\tau = 1/\Delta f_n$, where τ is the interpulse interval (10). Thus, when the required conditions are met, a train of "soft" pulses is applied to the sample which has a net effect of selectively tipping only one spin to a 90° flip angle followed by data sampling (11).

In the manner described, we were thus able to selectively excite the carbon resonances associated with the 4- and 6-positions of the 1-azaphenoxathiin ring system producing the set of sub-spectra shown in Figure 1. Measurement of the coupling constants for the individual resonances excited in this discrete manner thus removes any ambiguity and precludes the possibility of mismeasurement of coupling constants. In this fashion, using the selective excitation technique, the primary coupling constants have thus been determined to be incorrect in the original analysis of the gated decoupled spectrum through an unfortuitous mismatching of spin-multiplet halves. The correct and unequivocal values of the primary coupling constants for these resonances are shown in Table I.

The effectiveness of selective excitation/gated decoupling, as an aid in the analysis of complex gated decoupled ^{13}C-nmr spectra is clearly seen in this correction of the originally reported coupling constant data for 1-azaphenoxathiin. Its utilization in obtaining valuable structural information from the complex gated decoupled spectra of heteroaromatic systems as well as other hetero-

Table I

^{13}C-^{1}H Coupling Data for the 4- and 6-Positions of the 1-Azaphenoxathiin Ring System (**1**) Obtained by Selective Excitation/Gated Decoupling Techniques



1

Resonance	$^{1}J_{CH}$	$^{3}J_{CH}$
4	$^{1}J_{C_4H_4} = 163.7$	$^{3}J_{C_4H_2} = 8.4$
6	$^{1}J_{C_6H_6} = 162.3$	$^{3}J_{C_6H_8} = 7.1$

cyclic systems will probably be seen in the near future.

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(8) Typically, flip angles ranging from approximately 1.5° down to 0.3° are utilized in this procedure. Attenuation of the standard 90°, 20μsec pulse is conveniently achieved by a Varian Model V-4311 fixed frequency rf unit in line between the pulse amplifier and the probe of the spectrometer.

(9) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 94, 630 (1954).

(10) Direct calculation of the pulse intervals τ, according to the equation in the text failed to result in selective excitation on the Varian XL-100 spectrometer equipped with a Nicolet TT-100 data system used for these experiments. Rather, it was necessary to subtract a 1.6×10^{-5} sec correction from the calculated value of τ to achieve the desired selective excitation. The nature of the factors necessitating this correction are at present unknown but are undergoing further investigation.

(11) Pulse application under computer control was accomplished by the modification of the standard T_2 Carr-Purcell sequence given in the following equation: $|\{[P_1(D_1\text{--}P_2)_{EC}]$ sample and add$\}$ $D5|NA$; $P_1 = P_2 = 4\mu s$ pulse attenuated 21 dB; $D_1 = \tau(0.001547$ and 0.002170 sec for C_4 and C_6, respectively); EC = number of pulses applied (200); D_5 = delay between sequence executions (0.50 sec); NA = total number of acquisitions obtained (1000); Sweep width = 5 kHz; Acquisition time = 0.8192 sec; data = 8k.