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A REINTERPRETATION OF LONG-RANGE $^{13}C-^{1}H$ COUPLINGS IN FURANS

AN APPLICATION OF THE GASP-TECHNIQUE

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As part of a study of the influence of neighbouring bulky substituents on the chemical shifts of the carbon atoms of substituted furans[1], we measured the ^{13}C-NMR spectra[2] of furan (I), 2-methylfuran (II), 3-methylfuran (III), 2-t-butylfuran (IV), 3-t-butylfuran (V), 2,5-dimethylfuran (VI), 2,5-di-t-butylfuran (VII), 2,4-di-t-butylfuran (VIII) and 2-methyl-4-t-butylfuran (IX). The assignments of the ^{13}C-resonances of the monosubstituted furans II-V were based on the magnitudes of the long-range carbon-proton coupling constants in furans as presented by Weigert and Roberts[3].

By comparing the chemical shifts of furans II-V with that of furan itself, substituent effects can be calculated for methyl- and t-butyl-substituents. These values are collected in Table I.

TABLE I

Compound	Chemical shift difference (ppm) with respect to furan			
	C_2	C_3	C_4	C_5
II	9.1	-3.9	0.8	-1.9
III	0.1	10.0	2.7	-3.2
IV	21.2	-7.5	0.3	-2.0
V	0.1	26.4	-0.5	-5.8

The resonances of the disubstituted furans VI-IX could be assigned unequivocally because of the large difference in chemical shift of α- and β-furan carbons and due to the fact that quaternary carbon atoms always give lines with lower intensity than carbons bearing hydrogens.

From the results collected in Table I, the chemical shifts of furans VI-IX can also be calculated, by simply adding the different substituent effects. Since shift additivity is a general phenomenon in ^{13}C-NMR[4], it is expected, that calculated and observed shifts agree within the experimental error (0.2 ppm). From Table II it can be seen, that this is true for all the carbons of the 2,5-disubstituted furans VI and VII, but not for the 2- and 5-carbons of the 2,4-disubstituted furans VIII and IX.

TABLE II

Compound	Chemical shift (ppm) with respect to TMS											
	C_2			C_3			C_4			C_5		
	obs.	calc.	diff.	obs.	calc.	diff.	obs.	calc.	diff.	obs.	calc.	diff.
VI	148.8	148.7	0.1	105.3	105.5	-0.2	105.3	105.5	-0.2	148.8	148.7	0.1
VII	160.4	160.7	-0.3	101.2	101.4	-0.2	101.2	101.4	-0.2	160.4	160.7	-0.3
VIII	133.6	139.6	-6.0	135.0	135.3	-0.3	100.4	100.6	-0.2	162.9	156.9	6.0
IX	133.7	139.7	-6.0	135.8	135.8	0.0	104.4	104.2	0.2	150.6	144.8	5.8

If, however, the assignments of carbons 2 and 5 in the 3-substituted furans are reversed (table III) and the shifts for furans VI-IX are calculated from the new substituent effects, comparison of calculated and observed shifts shows that complete agreement now exists (Table IV).

TABLE III

Compound	Chemical shift difference (ppm) with respect to furan			
	C_2	C_3	C_4	C_5
III	-3.2	10.0	2.7	0.1
V	-5.8	26.4	-0.5	0.1

TABLE IV

Compound	Chemical shift (ppm) with respect to TMS											
	C_2			C_3			C_4			C_5		
	obs.	calc.	diff.	obs.	calc.	diff.	obs.	calc.	diff.	obs.	calc.	diff.
VIII	133.6	133.7	-0.1	135.0	135.3	-0.3	100.4	100.6	-0.2	162.9	162.8	0.1
IX	133.7	133.8	-0.1	135.8	135.8	0.0	104.4	104.2	0.2	150.6	150.7	-0.1

This result prompted us to find a method by which the carbon chemical shifts of the monosubstituted furans could be assigned unambiguously. To that end we applied a new NMR technique, that is basically a GAted SPin tickling technique that we called the GASP-technique. In a gated spin tickling experiment similar conditions as in homonuclear proton spin tickling are used, but the spin decoupler is only on during the pulse delay and off during acquisition of the FID. In this way coupling constants remain the same (as in gated noise decoupled spectra[5]) whereas the line intensities are changed due to disturbations of the spin state populations involved (comparable to the theory of INDOR[6]). An example is given for a CH group. This can be described as a simple AX system (fig. I). Irradiation of transition H_1 (the low-field ^{13}C-satellite in the proton spectrum) transports spin population from αα to ββ. This results in a decrease of the intensity of C_1 (the low-field part of the carbon doublet) and an increase of the intensity of C_2. Because cross relaxation from βα to αβ is important in ^{13}C-NMR, C_1 can appear as a negative peak, if the population of αβ becomes larger than that of αα. It is clear that irradiation of transition H_2 results in a decrease of C_2 and an increase of C_1.

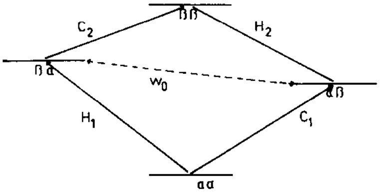
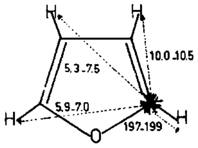
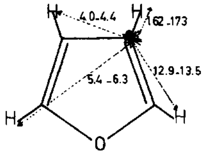


Figure 1

In more complicated spin systems it is possible to irradiate the ^{13}C-satellites caused by long-range ^{13}C-^{1}H coupling (often hidden under the normal proton signal). This results in asymmetry in the line heights of the long-range coupling pattern. An example of this technique has been worked out for fluorenone[7]. In our case the GASP-technique was used to assign the ^{13}C-lines of 2-t-butyl furan and 3-t-butyl furan, starting from the ^{13}C- satellites in the completely assigned proton spectra[8]. Irradiation of the low-field ^{13}C-satellite of the H_5-proton of 3-t-butylfuran (V) at δ=7.362 gives a negative peak for the low-field part of the carbon doublet at δ=141.6 and a 2.5 fold increase for the high-field part. If the ^{13}C-satellite of the H_2-proton at δ=7.220 is irradiated, the carbon doublet at δ=135.7 responds similarly. This means that the assignments as shown in table III are the correct ones. In a similar experiment it was shown that the ^{13}C-resonances of 2-t-butyl furan have to be assigned as already suggested in table I. It is to be expected that the GASP-technique will give results for primary and secundary carbon atoms as well whereby it is possible to obtain in a very selective way information on the connection between proton- and ^{13}C-spectra.

The results obtained from the furan spectra also mean that the original assignment of long-range couplings in furans as suggested by Roberts and Weigert[3] is not completely correct. We measured the long-range carbon-proton couplings (in Hz) of furans II-IX and the results are schematically given below:





It is noticeable that these furans present one of the few examples of aromatic heterocyclic compounds in which a $^2J_{CH}$ coupling is larger than a $^3J_{CH}$ coupling[9].

Acknowledgement

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References

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9. Ref. 4, pg. 101.