TABLE V

EXCHANGE OF N-ALLYLPYRIDINIUM FLUOROBORATE AT 25° WITH $\mathrm{H_2{}^3O}$ IN PRESENCE OF PYRROLIDINE

Salt concn., *M*	Base concn., *M*	Time, days	No. H's exchanged
0.046	None	7	0.0
0.068	0.031	6	4.1, 3.9

TABLE VI

VARIATION OF Q_1 WITH e_2 OF THE COMONOMER

Comonomer	Calcd. Q_1 for N-vinylpyridinium fluoroborate	e_2 of comonomer
Methyl methacrylate	0.31	0.4
Methyl acrylate	0.61	0.6
Acrylonitrile	1.9	1.2

tion 5 log Q_1 is seen to vary inversely with R_{12}, it follows that log Q_1 and e_2 will increase simultaneously, although not in direct proportion.

This conclusion is qualitatively supported by the data in Table VI. The indication is, therefore, that the simple assumption of constant R is not sufficiently accurate in this case.

It is interesting to note that the equation used by Barb and Ham[23,24] involving the penultimate group, that is

$$n - 1 = \frac{r_2'x(r_2x + 1)}{r_2'x + 1}$$

where n is the ratio of monomer 2 to monomer 1 in the copolymer, x is the ratio of monomer 2 to monomer 1 in the reaction mixture, $r_2 = k_{222}/k_{221}$ and $r_2' = k_{122}/k_{121}$, fits the experimental data less exactly than the standard copolymerization equation.

(23) W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953).

(24) G. E. Ham, *ibid.*, **55**, 169 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

Complete Analysis of the Proton Magnetic Resonance Spectrum of Furan by Means of C^{13}-H Patterns

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RECEIVED AUGUST 7, 1961

The n.m.r. spectrum of furan has been studied in acetone solution under conditions of very high resolution. The spectrum consists of two quartets, instead of the two triplets originally observed. Accurate and unambiguous values for all four coupling constants were obtained from the C^{13}-H spectrum, observed in natural abundance. With these results it was then possible to carry out an analysis of the entire spectrum of normal furan, leading to a calculated spectrum in good agreement with the observed spectrum. The values of the adjacent and cross-ring coupling constants obtained, 1.75 c.p.s. and 0.85 c.p.s., establish quite clearly that the early assumptions of the equality of these two coupling constants is not justified.

Introduction

The proton magnetic resonance spectra of furan, thiophene and pyrrole have been the subjects of a number of investigations in recent years,[1-7] in part directed toward the clarification of erroneous inferences originally derived from the simple spectral patterns of these heterocyclic compounds. According to early studies, the spectrum of thiophene consists of two closely-spaced triplets from which it was concluded that the *ortho* (adjacent) and *para* (cross-ring) coupling constants were equal. On this basis thiophene was considered as an A_2B_2 system. Subsequent investigations of thiophene in polar solvents, such as acetone and dimethyl sulfoxide, provided more complex patterns which were analyzed as AA'BB' systems with the result that the adjacent and cross-ring coupling constants were demonstrated to be unequal.

Furan has been studied in a variety of solvents. Its spectrum is strictly first-order, consisting of two rather widely separated triplets, which were originally interpreted on the basis of an assumed equality of adjacent and cross-ring coupling constants. Subsequently, Abraham and Bernstein[5] and Gutowsky, *et al.*,[8] called attention to another possible interpretation of these spectra. From the theoretical expressions for the allowed transitions in AA'BB' systems, which contain the coupling constants only as sums and differences, it can be shown that the observed triplet spacing of 1.3 c.p.s. in furan is actually half the sum of the adjacent ($J_{\text{adj.}}$) and cross-ring constants (J_{cross}). It is only on the assumption of an A_2B_2 system that the observed first-order triplet spacings provide the value of $J_{\text{adj.}} = J_{\text{cross}}$. If the system is actually AA'BB' it is impossible to determine separately the values of $J_{\text{adj.}}$ and J_{cross}, as well as the values of J_{AA} and J_{BB}, from the observed spectrum.

As a means of eliminating this indeterminacy, Abraham and Bernstein[5,6] adopted for furan the mean values of the appropriate coupling constants determined in a series of substituted furans, having shown that these values were roughly constant over the series. By this procedure they were able to obtain satisfactory agreement between the calculated and observed spectra of furan. However, since both hypotheses, *i.e.*, $J_{\text{adj.}} = J_{\text{cross}}$ and $J_{\text{adj.}} \neq J_{\text{cross}}$, led to satisfactory agreement with experiment, there was still no clear-cut basis for a choice between the two alternative interpretations. Moreover, it has been well established that n.m.r. coupling constants are more or less sensitive to substitu-

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(1) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

(2) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

(3) E. J. Corey, G. Slomp, S. Dev, S. Tobinaga and E. R. Glazier, *ibid.*, **80**, 1204 (1958).

(4) J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 518 (1955).

(5) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(6) R. J. Abraham and H. J. Bernstein, *ibid.*, **39**, 905 (1961).

(7) S. Gronowitz and R. A. Hoffman, *Arkiv. kemi.*, **13**, 279 (1958).

(8) D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961).

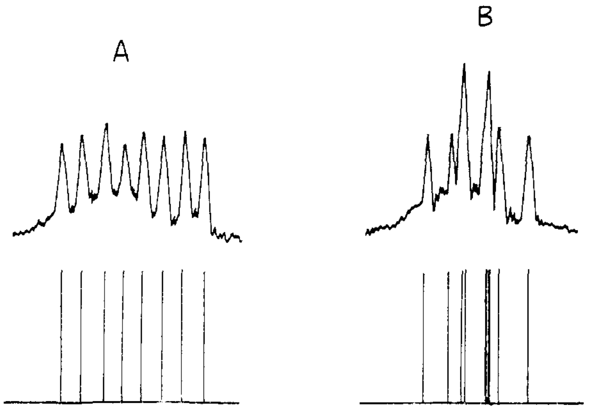


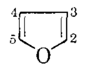
Fig. 1.—C^{13}-H spectra of furan: A, high field part of β-protons; B, low field part of α-protons. The lower parts are the calculated first order spectra.

tion at least in vinyl systems,[9] and in the case of small coupling constants even minor variations in magnitude produced by substituents can be troublesome. Even more serious is the possibility that, although the coupling constants do not vary widely with substituents, the values in unsubstituted furan itself could be rather different. For example, in thiophene the introduction of a substituent can alter the coupling constants by as much as 80%.[10] Thus, the value of J_{cross} in thiophene is 1.0 c.p.s., but the value in 2-bromothiophene is 1.8 c.p.s. In the 2-methyl, 2-chloro, 2-nitro and 2-iodo derivatives the cross-ring couplings fall between these two values. Similarly, variations of about 1.0 c.p.s. in J_{34} have been observed in the 2-substituted thiophenes, the smallest value of J_{34} occurring in thiophene itself. The situation in these thiophene derivatives indicates that some caution should be exercised in assuming that coupling constants can be transferred from derivatives of furan to furan itself.

This investigation has been directed toward obtaining an unambiguous solution of the problem of the n.m.r. spectrum of furan. As our first step, we obtained the spectrum of furan in acetone under sufficient resolution to show that it consisted of two quartets, rather than the two triplets heretofore reported. This spectrum is shown in Figs. 2 and 3. These quartet patterns prove conclusively that J_{cross} and $J_{\text{adj.}}$ are not equal. Unfortunately, not even this spectrum will provide reliable values of the couplings, since a great many alternative sets of values will lead to its correct prediction.

Accordingly, we have examined and studied the C^{13}-H spectrum of furan (in natural isotopic abundance). In this spectrum each proton attached to a C^{13} atom is displaced, upfield and downfield, by half the amount of the C^{13}-H coupling at that position. For the species containing C^{13} at either (equivalent) α position, the two α protons are so widely separated that the interaction between them is first-order. A similar situation exists between the two β protons for the species containing C^{13} and either (equivalent) β position. For each species, therefore, the C^{13}-H spectrum should be a first-order pattern, the proton attached to C^{13} being split by the other three protons to give an octet. Since in furan the β protons are at a higher field than the α protons, the upper half of β C^{13} doublet and the lower half of the α C^{13} doublet will be the more nearly pure first-order patterns and will be better separated from the principal spectrum of furan.

From the C^{13} (α) spectrum we can obtain the three coupling constants J_{25}, J_{23} ($=J_{45}$) and J_{24} ($=J_{35}$), defined by the labelling scheme



In similar fashion the C^{13} (β) spectrum gives the values of J_{34}, J_{23} and J_{24}. The fact that J_{23} (or $J_{\text{adj.}}$) and J_{24} (or J_{cross}) are involved in both C^{13} patterns provides an independent check for these two coupling constants, in addition to the agreement required in the principal spectrum.

Experimental

All the spectra were obtained on a Varian Model 4300B High Resolution Spectrometer operating at 40 Mc./sec. and equipped with a Flux Stabilizer. The furan used was the commercially available material, further purified by fractional distillation. The spectra were observed at about 10% concentration in acetone to which about 3% tetramethylsilane (TMS) was added to serve as an internal reference. For the C^{13}-H spectra pure furan was used with the triplet peak of normal furan used as a reference to calibrate the C^{13}-H spectra. The calibrations were carried out by the usual side-band technique, and the averages of eight measurements (four forward and four reverse) were obtained. The maximum deviation in the frequencies is 0.10 c.p.s., which can be taken as the maximum deviation in the chemical shifts and coupling constants. All the chemical shifts are expressed in c.p.s. at 40 Mc./sec. from tetramethylsilane (internal), and the coupling constants are directly expressed in c.p.s.

Results and Discussion

The C^{13}-H spectrum of furan is shown in Fig. 1; A is the high-field half of the H_β doublet and B is the low-field half of the H_α doublet. The observed chemical shifts from both patterns are given in Table I. The coupling constants derived by the first-order analysis of each pattern are listed in Table II, together with the values of the chemical shifts, ω_α and ω_β, obtained from the spectrum of normal furan. The uncertainty for all the coupling constants and chemical shifts is estimated to be less than 0.1 c.p.s. based upon agreement between calculated and observed spectra.

TABLE I

OBSERVED C^{13}-H SPECTRUM OF FURAN[a]

Peak no.	α-Protons[b]	β-Protons[c]
1	−102.7	84.7
2	−101.7	85.5
3		86.5
	−101.1	
4		87.3
5	−100.3	88.0
6		88.8
7	− 99.6	89.7
8	− 98.7	90.6

[a] In c.p.s. at 40 Mc./sec., relative to the center of the spectrum of the respective protons in normal furan. [b] Low-field half of C^{13}-H doublet. [c] High-field half of C^{13}-H doublet.

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(9) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **35**, 380 (1961).

(10) J. C. Randall, G. S. Reddy and J. H. Goldstein, unpublished results.

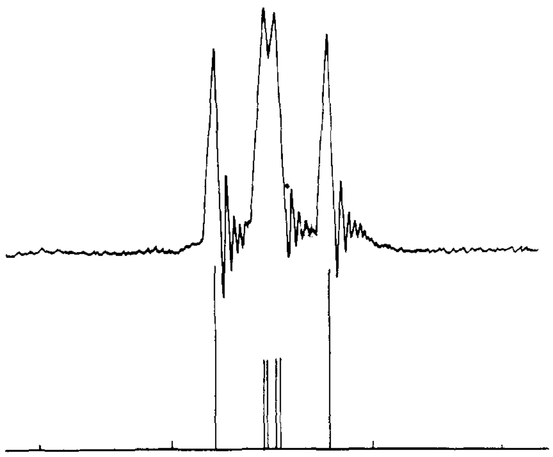


Fig. 2.—N.m.r. spectrum of furan in acetone: (*ca.* 10%) at 40 Mc./sec., α-protons. The lower part is the calculated spectrum.

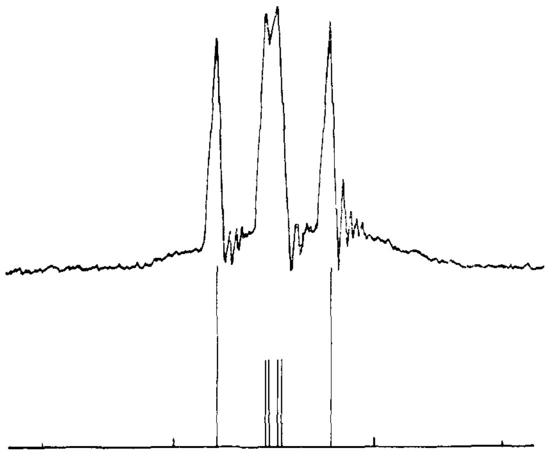
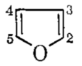


Fig. 3.—N.m.r. spectrum of furan in acetone: (*ca.* 10%) at 40 Mc./sec., β-protons. The lower part is the calculated spectrum.

The spectrum of the α protons in normal furan is shown in Fig. 2 and that of the β protons in Fig. 3. The observed and the calculated frequencies, based upon the parameters of Table II, for normal furan are given in Table III. It should be noted that the observed separations of 0.2 c.p.s. in the middle two peaks of both quartets are very adequately reproduced in the calculated spectrum and that the observed and calculated intensities agree very closely.

TABLE II

N.M.R. PARAMETERS FOR FURAN[a]



Parameter	From C^{13}-Hα	From C^{13}-Hβ	Average
J_{23}	1.7	1.8	1.75
J_{24}	0.9	0.8	0.85
J_{25}	1.4	...	1.4
J_{34}	...	3.3	3.3
$J(C^{13}\text{-H})$	201.4	175.3	
ω_α[b]	−291.9		
ω_β[b]	−250.0		

[a] All values in c.p.s. [b] Obtained from the data in Table III.

The average values of the coupling constants J_{23} = 1.75 c.p.s. and J_{24} = 0.85 c.p.s. demonstrate conclusively that the previously discussed assumption of equality of the adjacent and cross-ring couplings is not valid. However, these two values are essentially identical (within 0.1 c.p.s.) with the corresponding average values obtained by Abraham and Bernstein for a series of substituted furans.[6] The average values reported by these authors for the other two coupling constants, J_{25} = 1.55 c.p.s. and J_{34} = 3.53 c.p.s., differ from the present values by 0.15 and 0.23 c.p.s., respectively. On the whole, therefore, it appears that coupling constant values averaged over a series of substituted furans are in reasonably good, though not exact, agreement with the values obtained in this investigation.

The following advantages are afforded by the use of the additional data provided by the C^{13}-H spectrum of furan; ambiguities in the assignment of coupling constants are eliminated; the coupling constants can be evaluated more accurately, usually to 0.1 c.p.s. or better; and internal checks for most of the coupling constant values are available.

TABLE III

CALCULATED AND OBSERVED SPECTRUM OF FURAN[a]

Peak	Frequency Calcd.	Frequency Obsd.	Intensity Calcd.	Intensity Obsd.
		α-Peaks		
1	−296.65	.....	0.01	..
2	−293.93	.....	0.05	..
3	−293.20	−293.2	1.00	2.00
4	−293.20		1.00	
5	−292.03	−292.0	0.94	2.00
6	−291.95		.94	
7	−291.85	−291.8	.99	2.00
8	−291.77		.94	
9	−290.60	−290.6	1.00	2.00
10	−290.60		1.00	
11	−298.87	.....	0.05	..
12	−287.15	...	.01	..
		β-Peaks		
1	−254.75	...	0.01	..
2	−252.03	...	.05	..
3	−251.30	−251.30	1.00	2.00
4	−251.30		1.00	
5	−250.13	−250.10	0.99	2.00
6	−250.05		.94	
7	−249.95	−249.90	.99	2.00
8	−249.87		.94	
9	−248.70	−248.7	1.00	2.00
10	−248.70		1.00	
11	−247.97	.....	0.05	..
12	−245.25	...	.01	..

[a] All frequencies are in c.p.s. at 40 Mc./sec., in dilute (*ca.* 10%) solution in acetone, relative to TMS (tetramethylsilane) internal reference.

Acknowledgments.—The authors wish to thank Mr. J. C. Randall for his assistance in several phases of this study. They are indebted to the National Institutes of Health and to Schering Corporation for grants supporting much of the work reported here.