

The general conclusion is that, in equilibria between analogous silicon and carbon cations and their molecular precursors, there is an approximately equal tendency for the silicon or carbon cation to be formed, except when unusually strong bonds to silicon must be broken to form the cation. In the latter case the carbonium ion will be thermodynamically favored.

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## The Carbon-13 Nuclear Magnetic Resonance Spectra of Furan, Pyrrole, Thiophene, and Some of Their Methyl Derivatives<sup>1a</sup>

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*The 15.085 Mc.p.s. C<sup>13</sup> nuclear magnetic resonance spectra of furan, pyrrole, thiophene, and their 2-methyl and 2,5-dimethyl derivatives have been obtained and completely assigned. The assignment of the chemical shift data was based on C<sup>13</sup>-H coupling constants in the parent compound and on the proton-induced multiplet structure in the dimethyl compounds. The initial assignment of chemical shift values for the 2-methyl series was based on additive substituent relationships and C<sup>13</sup>-H coupling constants. These assignments were confirmed unequivocally with the proton-decoupling technique. Aromatic character in these compounds is inferred from the similarity of the corresponding chemical shift values with those of the ordinary benzenoid aromatics. Failure of the chemical shift data to correlate in every detail with estimates of the  $\pi$ -electron charge densities argues for the importance of  $\sigma$ -bond effects.*

### Introduction

The proton magnetic resonance spectra of furan, pyrrole, and thiophene as well as many of their derivatives have been studied extensively, and many of their n.m.r. spectral parameters have been correlated with such substituent properties as electronegativity and magnetic anisotropy.<sup>2-6</sup> In particular methyl substitution effects have received attention.<sup>7</sup> A close cor-

relation between C<sup>13</sup> chemical shifts and  $\pi$ -electron densities for both benzenoid and nonbenzenoid aromatic molecules has been noted experimentally<sup>8-12</sup> and theoretical justification for this correlation has been presented.<sup>13,14</sup>

It is widely accepted that furan, pyrrole, and thiophene all possess aromaticity in varying degrees, and this study has been undertaken to explore possible correlations between the carbon-13 chemical shift values and calculated  $\pi$ -electron charge distributions. To aid in the spectral interpretation of the parent compounds and to study the effects of methyl substitution, the C<sup>13</sup> spectra of the 2-methyl and 2,5-dimethyl derivatives were also examined. Previous work by Spiesecke and Schneider<sup>15</sup> and Grant and Paul<sup>16</sup> has shown that the introduction of a methyl group into an alkane will shift the resonance of a directly bonded carbon-13 nucleus down field by approximately 9 p.p.m. provided that the carbon atom is not at a center of high branching. Shifts of similar magnitudes were found in this study, whereas no previous values have been published which will rationalize the remote methyl substituent effects recorded in this paper.

### Experimental Section

*A. Rapid-Passage Spectra.* These spectra were obtained at 15.085 Mc.p.s. on a Varian HR-60 spectrometer operating in the dispersion mode. Both adiabatic "rapid" and "intermediate" passage conditions

(1) (a) This paper is considered to be the first in a series from the Battelle Memorial Institute and no. IV in the series from the laboratory at the University of Utah. Previous paper in this later series: R. J. Pugmire, D. M. Grant, R. K. Robins, and G. W. Rhodes, *J. Am. Chem. Soc.*, **87**, 2225 (1965); (b) National Science Foundation Cooperative Fellow 1964-1966.

(2) (a) S. Gronowitz, G. Sorbin, B. Gestblom, and R. A. Hoffman, *Arkiv Kemi*, **19**, 438 (1962); (b) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961).

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were employed with sweep rates of about 0.5 and 0.15 gauss/min., respectively. The 10-mm. o.d. thin-walled sample tubes obtained from the Wilmad Glass Co. were spun at a rate of about 35 r.p.s. using a spinner from the same source. To inhibit the formation of a vortex a cylindrical nylon plug was positioned at the liquid-air interface. The signal to noise ratio was improved by using the 2000-c.p.s. field modulation and phase sensitive detector of a Varian Associates Model V-3521A integrator operating on the side-band mode in accordance with the general technique described by Anderson and Acrivos.<sup>17a,b</sup>

The rapid-passage data were obtained for a sample concentration of 70% in CS<sub>2</sub>. The signal from CS<sub>2</sub> is used as an internal reference and calibrated sweep rates were obtained from the usual side-band technique on neat CS<sub>2</sub> solutions. Because of the asymmetry introduced by rapid passage dispersion mode conditions, all measurements are the average of at least six scans (three increase and three decrease). For sweeps of 100 p.p.m. or more the chemical shift scale was calibrated by running acetic acid before and after each scan. The separation in the carbonyl and methyl resonance positions was taken to be 158.0 p.p.m. Shorter sweeps were calibrated with the 130-c.p.s. splitting in the methyl quartet of acetic acid. Chemical shifts obtained from the two methods were reproducible to  $\pm 0.5$  and  $\pm 0.3$  p.p.m., respectively.

The dispersion mode spectra are given in Figures 1-9. In each case both an increase and decrease scan are shown, with the increase scan on top. The frequencies (in c.p.s. vs. internal CS<sub>2</sub>) noted in the figures are the averages of the six or more scans noted above.

**B. Proton Decoupled Spectra.** Operating at the same transmitter frequency the proton decoupled carbon-13 spectra were obtained in the manner described by Paul and Grant<sup>18</sup> with the use of a Varian V-4320 heteronuclear spin decoupler operating at 60 Mc.p.s. The samples were run as neat liquids using 12-mm. sample tubes which are spun with a Wilmad spinner assembly. The frequency of both the transmitter and proton decoupler was measured with an accuracy of  $\pm 1$  c.p.s. with a Hewlett-Packard 524C electronic counter equipped with a 525A frequency converter. Peak enhancements resulting from proton decoupling techniques allows the spectra to be obtained at non-saturating H<sub>1</sub> power levels on the absorption mode under slow passage conditions. By determining accurately the carbon-13 transmitter and proton decoupling frequencies it is possible to determine<sup>18</sup> the carbon-13 chemical shift values with a precision of about  $\pm 0.07$  p.p.m.

**C. Compounds.** Except for 2-methylpyrrole and 2-deuteriothiophene all compounds were obtained from commercial sources and used without purification. Purity was checked by running the proton n.m.r. spectra and also by gas-liquid partition chromatography in the furan series.

**2-Methylpyrrole.** A stirred mixture of 9.5 g. of pyrrole-2-carboxaldehyde, 20 g. of KOH, 13 ml. of hydrazine (95+%), and 130 ml. of diethyleneglycol

was heated slowly. The material then was distilled below 190° (mostly between 140 and 180°), diluted with water, and extracted with ether. The ether solution was dried with MgSO<sub>4</sub>, stripped, and redistilled at atmospheric pressure. The fraction distilling between 146 and 148° (4.1 g.) was collected. The boiling point reported in the literature<sup>19</sup> is 148°.

**2-Deuteriothiophene.** This compound was obtained by treating the corresponding magnesium iodide Grignard reagent with deuterium oxide. The 2-iodothiophene, from which the Grignard is prepared, was synthesized according to a standard preparation.<sup>20</sup>

## Spectral Assignment

**A. Parent Compounds.** The rapid-passage spectra for furan, pyrrole, and thiophene are contained in Figures 1, 2, and 3, respectively. The spectrum in each case consists of four lines resulting from proton-induced doublets in the resonance of the  $\alpha$ - and  $\beta$ -carbon atoms. The lines in these two multiplets can be assigned to the respective nuclei from the magnitudes of the directly bonded proton-carbon-13 coupling constants which have been published by Tori and Nakagawa<sup>21</sup> for a large number of heteroaromatic molecules. In all of the compounds studied the proton splitting is larger in the  $\alpha$ -carbon adjacent to the heteroatom than in the  $\beta$ -position. Thus, positions C-2 and C-5 may be distinguished from positions C-3 and C-4 for those compounds in which a proton is directly bonded to the carbon atom under study.

While the multiplets are easily recognized and identified in the furan spectrum, it is helpful with the use of proton decoupling to remove any ambiguities in the assignment of the closely positioned spectral lines in thiophene and pyrrole. Elimination of the proton splitting in these two compounds gave spectra with singlet lines positioned at the midpoint of each of the two doublets found in the original spectra. The chemical shifts of the  $\alpha$ - and  $\beta$ -carbons in thiophene are very similar in magnitude as well as being reversed in order from that noted for furan and pyrrole. Thus, the spectrum of 2-deuteriothiophene was secured to corroborate the initial assignment based on the magnitude of the coupling constants. Replacement of the proton at C-2 with deuterium causes the C-2 resonance to be broadened appreciably due to the quadrupole relaxation of and spin coupling with the H<sup>2</sup> nucleus. Therefore, under the conditions of proton decoupling, the resonance of C-2 is not observed. The decoupled spectrum thus consisted of a two-line spectrum with intensities of 2 to 1 for the  $\beta$ - and  $\alpha$ -carbons, respectively. This work confirmed the assignment of the high field doublet to C-2 and C-5.

The difference in the appearance of the two center lines in the pyrrole spectrum (see Figure 2) obtained for increasing and decreasing field sweeps possibly is due to a combination of nonequivalent magnetization transfer in the two multiplets and to slightly different line widths. With an increasing sweep, it was not possible to resolve the broader and less intense high-field line of the  $\alpha$ -multiplet from the sharper and more intense, low-field peak of the  $\beta$ -multiplet. However, under de-

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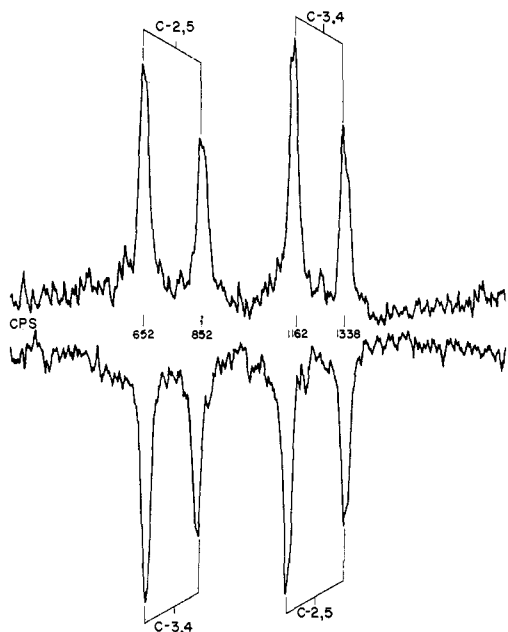


Figure 1. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of furan.

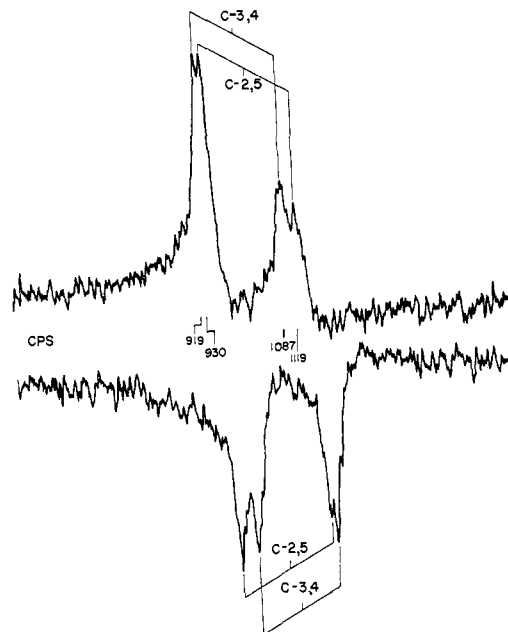


Figure 3. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of thiophene.

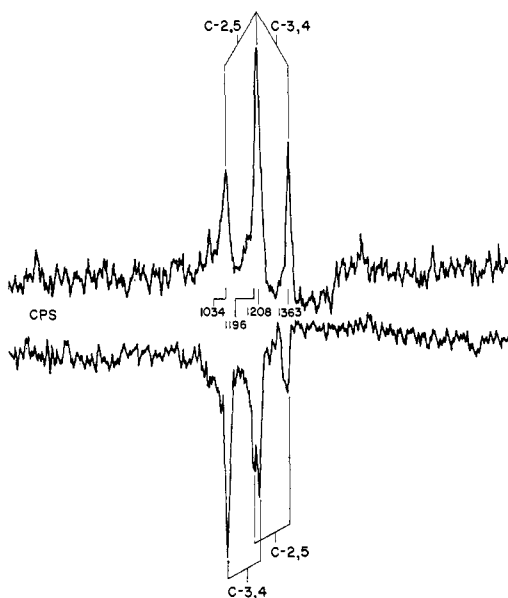


Figure 2. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of pyrrole.

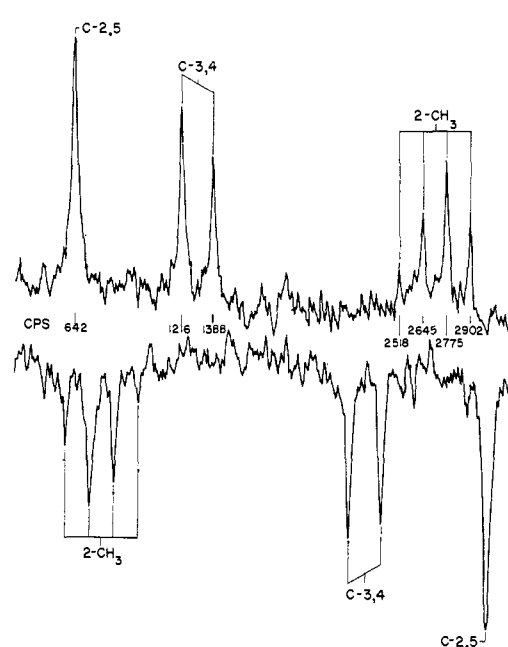


Figure 4. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2,5-dimethylfuran.

creasing field conditions the low-field line of the  $\beta$ -doublet is narrower and although its intensity has been attenuated by magnetization transfer it nevertheless is distinguishable as a shoulder on the more intense high-field peak of the  $\alpha$ -multiplet. All coupling constants obtained from rapid-passage data recorded for pyrrole are taken from decreasing field sweep spectra where all four main peaks are observable. Contained in Table I are the chemical shifts and coupling constants for the three parent compounds and some of their methyl derivatives.

**B. 2,5-Dimethyl Compounds.** The spectra for this series of compounds are assigned from the multiplet structure observed under rapid passage conditions as shown, respectively, in Figures 4, 5, and 6 for the 2,5-dimethyl derivatives of furan, pyrrole, and thiophene. In all three compounds the strong singlet due to C-2

and C-5 is at the lowest field, the C-3 and C-4 doublet appears next, and shifted up field by approximately 100 p.p.m. is the characteristic methyl quartet. Agreement of the observed splittings in this series of compounds with literature values for the proton-carbon-13 coupling constants further confirms the assignments for the furan and thiophene derivatives. The couplings for 2,5-dimethylpyrrole, where literature values are unavailable, are close to those which might be expected from similar values in related compounds.

**C. 2-Methyl Compounds.** The spectra of the 2-methyl derivatives of furan, pyrrole, and thiophene are given in Figures 7, 8, and 9, respectively. As found in the previous dimethyl series the C-2 singlet and the

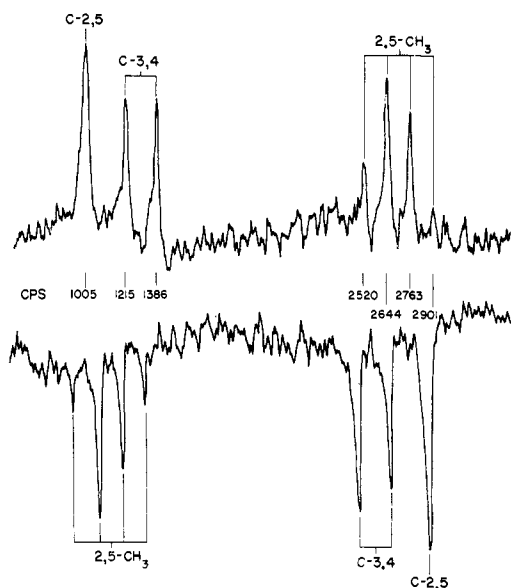


Figure 5. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2,5-dimethylpyrrole.

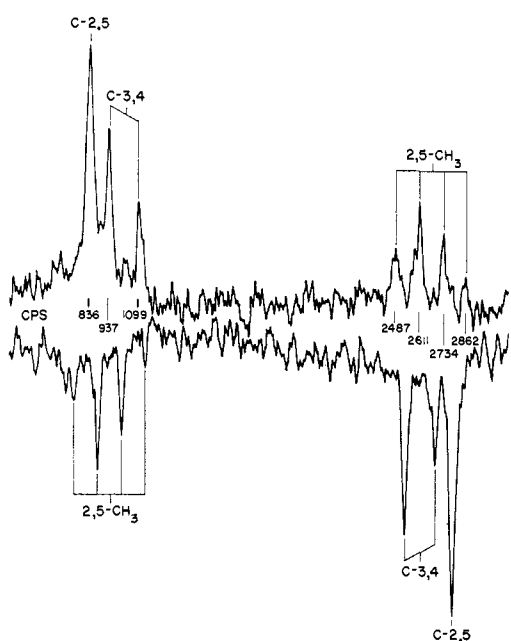


Figure 6. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2,5-dimethylthiophene.

methyl quartet can be assigned from the multiplet structure. Singlets are readily recognized in rapid passage spectra as their intensity<sup>22</sup> is the same in both forward and reverse field sweeps. In the remaining positions (C-3, C-4, and C-5) effective use is made of proton decoupling to relate the six interlaced lines (see Figures 7-9) with the three decoupled singlets appearing at the midpoint of each doublet. This was particularly helpful in the spectrum of 2-methylpyrrole in which the high-field C-5 line and low-field C-3 line coalesce. After the three pairs of lines had been identified, the one pair with the greatest separation is assigned to C-5 on the basis that the proton-carbon-13 coupling constant is the largest in the  $\alpha$ -position. Coupling con-

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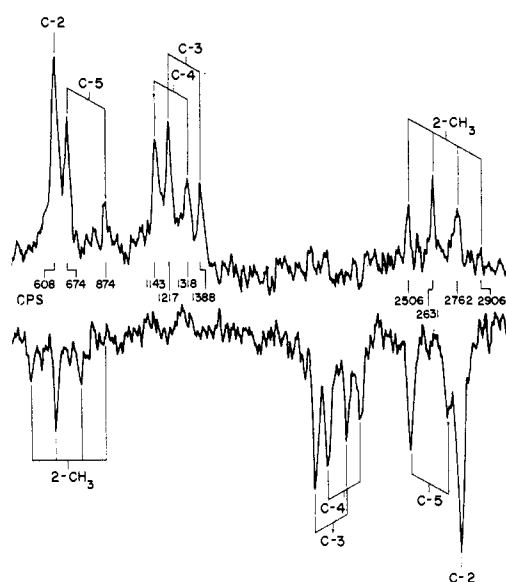


Figure 7. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2-methylfuran.

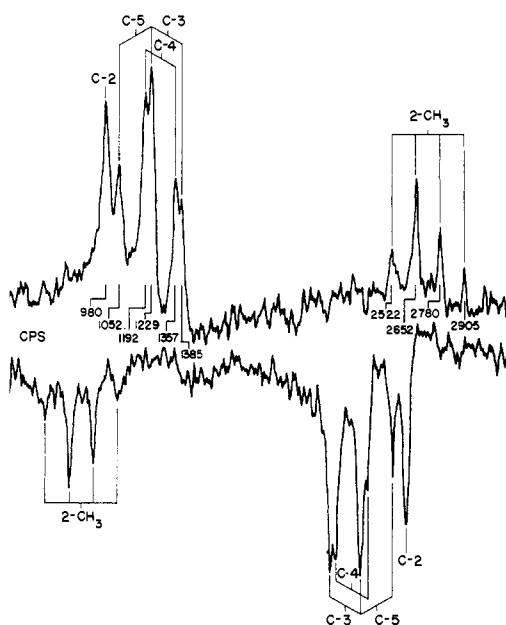


Figure 8. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2-methylpyrrole.

stants of 200, 177, and 186 c.p.s. at the 5-position in the 2-methyl derivatives compare favorably with the corresponding  $\alpha$ -couplings measured from the proton spectra of furan (200 c.p.s.), pyrrole (182 c.p.s.), and thiophene (189 c.p.s.), respectively.<sup>21</sup>

The assignment of the remaining two doublets to C-3 and C-4 cannot be based on the magnitudes of the splittings which are very similar for the two  $\beta$ -carbon atoms. However, from the slow sweep decoupling data and proton chemical shifts presented in Table I, one can check the correctness of a carbon-13 assignment by calculating the carbon-13 chemical shifts for all possible combinations of assignments of the three decoupled resonances to C-3, C-4, and C-5. The chemical shifts which result for the six possible assignments are calculated from the following equation<sup>18</sup>

$$\delta_C = 1 - \left(\frac{f_0}{\nu_0}\right) \left(\frac{\nu_i}{f_i}\right) (1 - \delta_H)$$

**Table I.** Carbon-13 Chemical Shift and Proton-Carbon-13 Coupling Constants of Selected Heterocyclic Compounds

Compd.	Position	Decoupler frequency, <sup>a</sup> c.p.s.	Proton chemical shift relative to TMS <sup>b</sup>	C <sup>13</sup> chemical shift values, p.p.m.			J <sub>13C-H</sub> , c.p.s.	
				Decoupling values <sup>c</sup> relative to C <sub>6</sub> H <sub>6</sub>	Rapid-passage values <sup>e</sup> relative to CS <sub>2</sub>		This study	Lit. values <sup>h</sup>
					This study	Lauterbur <sup>f</sup>		
Furan	2,5	59,983,008	7.32	-14.05	+49.8 (-15.0)	+50.6	200	201.4
	3,4	59,984,921	6.25	+18.94	+82.9 (+18.1)	+83.6	176	175.3
2-Methylfuran	2	...	...	-23.3 <sup>d</sup>	+40.3 (-24.5)	...	...	...
	3	59,985,142	5.88	+22.97	+86.3 (+21.5)	...	171	172.4
	4	59,984,870	6.17	+18.17	+81.6 (+16.8)	...	175	172.8
	5	59,983,104	7.18	-12.29	+51.3 (-13.5)	...	200	200.4
	Me	59,990,485	2.17	+115.75	+179.1 (+115.3)	...	133	126.4
2,5-Dimethylfuran	2,5	...	...	-21.4 <sup>d</sup>	+42.6 (-22.2)	...	...	...
	3,4	59,985,100	5.73	+22.27	+86.3 (+21.5)	...	172	169.8
	Me	59,990,482	2.17	+115.58	+179.6 (+115.8)	...	128	127.3
Pyrrole	2,5	59,984,401	6.42	+10.02	+74.4 (+9.6)	+74.4	182 <sup>g</sup>	184.0
	3,4	59,985,011	6.20	+20.29	+84.8 (+20.0)	+84.6	170 <sup>g</sup>	169.8
2-Methylpyrrole	2	...	...	+1.3 <sup>d</sup>	+65.0 (+0.2)	...	...	...
	3	59,985,114	5.80	+22.59	+86.7 (+21.9)	...	158	...
	4	59,984,996	6.03	+20.39	+84.5 (+19.7)	...	166	...
	5	59,984,493	6.29	+11.75	+75.6 (+10.8)	...	177	...
	Me	59,990,492	1.93	+116.09	+181.0 (+116.2)	...	128	...
2,5-Dimethylpyrrole	2,5	...	...	+2.7 <sup>d</sup>	+66.6 (+1.8)	+66.9	...	...
	3,4	59,985,102	5.67	+22.53	+86.2 (+21.6)	+86.9	171	...
	Me	59,990,482	2.03	+115.82	+179.6 (+114.8)	+179.9	127	...
Thiophene	2,5	59,984,016	7.04	+3.06	+67.9 (+3.1)	+66.9	189	184.5
	3,4	59,983,903	6.92	+1.28	+66.4 (+1.6)	+66.3	168	167.5
2-Methylthiophene	2	...	...	-10.7 <sup>d</sup>	+53.4 (-11.4)	...	...	...
	3	59,983,976	6.60	+3.02	+67.7 (+2.9)	...	164	163.6
	4	59,983,894	6.73	+1.49	+66.2 (+1.4)	...	170	165.5
	5	59,984,129	6.82	+5.32	+69.6 (+4.8)	...	186	184.9
	Me	59,990,368	2.29	+113.68	+178.1 (+113.3)	...	129	128.3
2,5-Dimethylthiophene	2,5	...	...	-8.7 <sup>d</sup>	+55.4 (-9.4)	+57.1	...	...
	3,4	59,983,999	6.40	+3.40	+67.5 (+2.7)	+67.7	162	161.2
	Me	59,990,362	2.25	+113.60	+177.6 (+112.8)	+178.4	125	128.2

<sup>a</sup> These values correspond to a constant transmitter frequency of 15,084,775 c.p.s. <sup>b</sup> These values are for neat liquids with only a small amount of TMS added as a standard. In calculating carbon-13 chemical shift values relative to benzene the chemical shift between TMS and benzene was taken to be 7.17 p.p.m. (Note: The carbon-13 and proton chemical shift scales run in opposite field directions.) <sup>c</sup> Samples were neat liquids and therefore data are referenced relative to external neat benzene which has a proton to carbon-13 frequency ratio of 3.976-4492 ± 0.0000004. <sup>d</sup> These values are obtained under slow sweep conditions from calibrated sweep rates. Error is estimated at ±0.2 p.p.m. <sup>e</sup> Values in parentheses are relative to benzene. The chemical shift of benzene relative to CS<sub>2</sub> is taken to be +64.8 p.p.m. The difference between the rapid passage and proton-decoupled values may be due to intrinsic errors and solvent effects. <sup>f</sup> P. C. Lauterbur, private communication. <sup>g</sup> Pyrrole coupling constants are taken from decreasing sweep data where all four peaks are observable. <sup>h</sup> Taken from ref. 21.

**Table II.** Comparison of Chemical Shift Data as Determined by Decoupling and Calibrated Sweep Methods

Compd.	Low-field peak		Mid-field peak		High-field peak		δ <sub>H</sub> - δ <sub>M</sub> / δ <sub>M</sub> - δ <sub>L</sub>	Experimental value, <sup>b</sup> δ <sub>H</sub> - δ <sub>M</sub> /δ <sub>M</sub> - δ <sub>L</sub>
	Carbon no.	δ <sub>L</sub> <sup>a</sup>	Carbon no.	δ <sub>M</sub> <sup>a</sup>	Carbon no.	δ <sub>H</sub> <sup>a</sup>		
2-Methylfuran	5	-12.29	4	+18.17	3	+22.97	0.158	0.154 ± 0.007
	5	-12.29	3	+18.46	4	+22.68	0.137	
	4	-11.28	5	+17.16	3	+22.97	0.204	
	4	-11.28	3	+18.46	5	+21.67	0.108	
	3	-10.99	4	+18.17	5	+21.67	0.120	
2-Methylpyrrole	3	-10.99	5	+17.16	4	+22.68	0.196	0.262 ± 0.013
	5	+11.75	4	+20.39	3	+22.59	0.255	
	5	+11.75	3	+20.62	4	+22.36	0.196	
	4	+12.01	5	+20.13	3	+22.59	0.303	
	4	+12.01	3	+20.62	5	+22.10	0.172	
2-Methylthiophene	3	+12.24	4	+20.39	5	+22.10	0.210	1.44 ± 0.06
	3	+12.24	5	+20.13	4	+22.36	0.283	
	4	+1.49	3	+3.02	5	+5.32	1.50	
	3	+1.62	4	+2.89	5	+5.32	1.91	
	5	+1.40	3	+3.02	4	+5.41	1.48	
	3	+1.62	5	+2.80	4	+5.41	2.21	
	4	+1.49	5	+2.80	3	+5.54	2.09	
	5	+1.40	4	+2.89	3	+5.54	1.78	

<sup>a</sup> Chemical shift in p.p.m. from benzene obtained from the frequencies of the transmitter and decoupler and the corresponding proton chemical shift. <sup>b</sup> Experimentally measured values obtained from proton-decoupled singlets under slow sweep conditions. Error limits are one standard deviation in the determination of this value obtained from a large number of spectra.

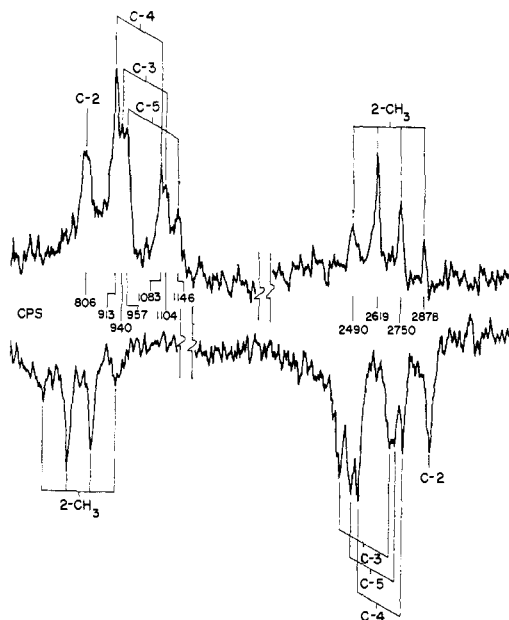


Figure 9. 15.085 Mc.p.s.  $C^{13}$  n.m.r. spectrum of 2-methylthiophene.

where  $\delta_C$  is the carbon chemical shift in p.p.m.,  $\delta_H$  is the chemical shift of the attached hydrogen in p.p.m.,  $f_i$  and  $\nu_i$  are, respectively, the resonance frequencies of the  $i$ th set of hydrogen and carbon-13 nuclei and  $f_0$  and  $\nu_0$  are the hydrogen and carbon-13 resonance frequencies of the reference compound which in this case is benzene. From the above equation it can be seen that the correct value of  $\delta_C$  will be calculated only when the correct value of  $\delta_H$  is used.

The carbon-13 shifts calculated for each of the six possible assignments of C-3, C-4, and C-5 are contained in Table II. In the next to last column of Table II are the calculated ratios of the relative separations of the three decoupled resonances. The experimentally determined ratios are entered in the last column. Because of the dependence of carbon-13 chemical shifts determined by slow-sweep decoupling techniques upon hydrogen chemical shifts, the experimental and calculated ratios will in general agree only if the carbon-13 doublets and the associated protons which induce the splitting are assigned correctly. It is therefore obvious that the carbon-13 assignment becomes dependent upon a correctly assigned and individually distinguishable set of proton shift values. Less obvious, however, is the further requirement that a certain asymmetry<sup>23</sup> must exist between the line positions in the carbon-13 and proton spectral region in order that alternative assignments may be distinguished from one another. When this asymmetry is lacking, other interpretive information is required.

In the furan and pyrrole compounds agreement between the two ratios is realized for only one permutation. In each of these cases the assignment is consistent with that based on spin-spin coupling data in which the low-field doublet is assigned to C-5. Furthermore, in both of these compounds it is possible to distinguish clearly between the alternative permutation of C-3 and

(23) This requirement is not always necessary if absolute shift values can be obtained from calibrated sweep data. However, for carbon-13 methods relative separations between three or more peaks are usually obtainable with greater accuracy.

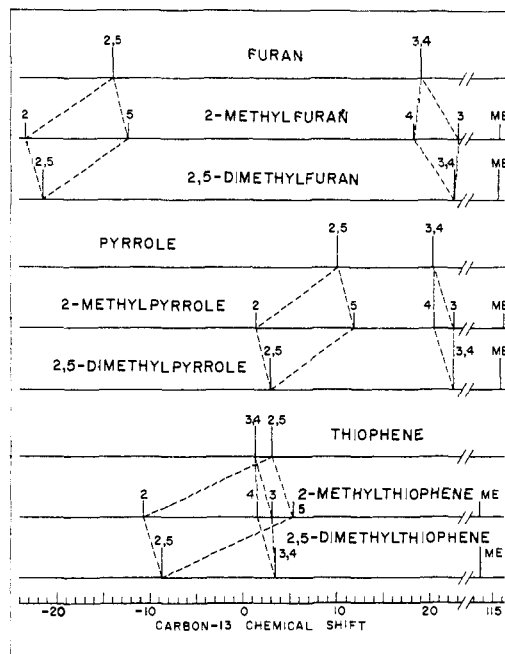


Figure 10. The additive effects of methyl substitution on the various ring carbons of five-membered heterocyclics.

C-4 which is the critical differentiation to be made. In the spectrum of 2-methylthiophene the relative spacings in both the carbon-13 and proton spectra are such that agreement between the two ratios is found for two of the six possible assignments. Fortunately, one of these possibilities can be eliminated on the basis of the coupling constant data which predict the C-5 doublet to be at highest field. Furthermore, the additive effects discussed in the next section hold only for the selected assignment. A calibrated sweep rate, which can be used to measure peak separations with an accuracy better than 0.09 p.p.m., would also have resolved the assignment. The 2-methylthiophene spectrum offers an example of both the limitation and the advantage of the decoupling method for making assignments. It does differentiate between the critical exchange of C-3 and C-4 although it is unable to make an unequivocal assignment if the question of the C-5 position is included in the problem.

One can also reach a consistent set of assignments based on rapid-passage data for the 2-methyl derivatives if it is assumed that the carbon-13 chemical shifts parallel the proton chemical shifts which have been reported.<sup>7</sup>

## Discussion

Figure 10 portrays schematically the effects of methyl substitution, and the additive features observed for these compounds can be observed from the parallelogram relationships which exist between the three members in each heterocyclic series. Table III summarizes the additive methyl substituent parameters of the respective ring positions if the methyl group is placed arbitrarily at C-2. Each entry is the mean of the substituent shifts recorded for the mono- and dimethyl compounds and the standard deviations for two samples becomes  $1/\sqrt{2}$  of the difference between the two values.

**Table III.** The Effect of Methyl Substitution at the 2-Position (p.p.m.)

Position	Furan		Pyrrole		Thiophene	
	Value	Error	Value	Error	Value	Error
C-2	-9.18	±0.10	-8.88	±0.23	-13.89	±0.18
C-3	+4.06	±0.05	+2.22	±0.11	+1.82	±0.12
C-4	-0.74	±0.05	+0.02	±0.11	+0.29	±0.12
C-5	+1.83	±0.10	+1.56	±0.23	+2.13	±0.18
5-Me <sup>a</sup>	-0.17	±0.07	-0.27	±0.07	-0.08	±0.07

<sup>a</sup> Error in this value is taken to be the intrinsic error in the proton-decoupling method as only a single datum is available in each case.

It is noted from Table III that the substituent effects for all three classes of compounds have comparable values, and all have the same sign with the exception of the effect at C-4 which is small in magnitude. The similarity noted in each of these classes of compounds supports the supposition that methyl perturbation on the electronic structure is remarkably similar in all of these molecules. The 9- to 13-p.p.m. shift to lower field at the  $\alpha$ -carbon is about the same as found in the alkanes.<sup>15, 16</sup> However, the remote substituent effects at the remaining positions fail to show analogous features, and it is evident that interaction between remote carbon atoms is different for the alkanes and these heterocyclics. Whereas the effect of coiling is probably important in the alkanes, this is not possible in the heterocyclics, and it is likely that electrostatic effects are required to explain substituent shifts.

Figure 11 contains a plot of carbon-13 vs. proton chemical shifts for directly bonded carbon-13 and hydrogen nuclei. A least-squares fit of the 18 points yielded a regression line with the equation  $\delta_{C^{13}} = -22.24\delta_{H^1} + 152.50$  which is drawn in Figure 11. The point corresponding to benzene (open square) has been included for the purpose of comparison. While the correlation is not perfect, it is evident that the same shielding effects are operative for both nuclei. From the above equation it can be seen that the carbon-13 chemical shifts are about 22 times greater than the corresponding proton shifts. Considering experimental variation, this factor is very close to that found by Spiess and Schneider<sup>12</sup> for the carbon-13 and proton chemical shifts in the *para* position of monosubstituted benzenes where chemical shift values have been related to Hammett  $\sigma$  constants. The similarity to phenyl systems suggests that the chemical shifts in heteroaromatic compounds are domi-

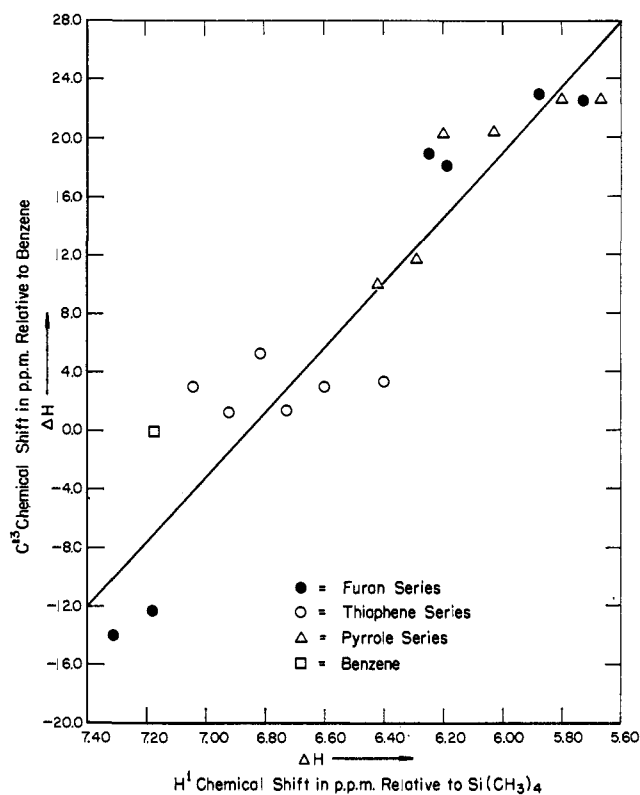


Figure 11. Plot of  $C^{13}$  chemical shifts in p.p.m. relative to benzene vs. the chemical shift of the attached proton in p.p.m. relative to  $Si(CH_3)_4$ . Data are taken from Table I.

nated by changes in the  $\pi$ -electron charge distribution. While it is possible to select several of a large number of theoretical treatments which will predict the proper charge dependence of the carbon-13 shifts, this was not felt to be significant because of the poor agreement between the various theoretical approaches. Furthermore, it is felt that the scatter in Figure 11 indicates the importance of  $\sigma$ -bond corrections on the  $\pi$ -electron terms.

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