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A series of *m*- and *p*-substituted 1-phenyl, 1-benzyl, 1-benzoyl, and 1-(2-phenylethyl)pyrroles was prepared and their ^1H and ^{13}C nmr spectroscopic characteristics were examined. In general, good correlations were observed between the chemical shift values of the β -H and the β -C of pyrroles [except 1-(2-phenylethyl)pyrroles] and the Hammett σ . The observation may be explained in terms of the electronic effects of the substituents which are transmitted through bonds and through space by interaction of the p orbitals between β -Cs of the pyrrole ring and *m*- and *p*-Cs of the phenyl ring. Substituent constants of 1-pyrrolyl, 1-pyrrolylmethyl, and 1-pyrrolyl groups for the ^1H and ^{13}C chemical shifts of phenyl ring are also presented.

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Nuclear magnetic resonance spectroscopy has been widely used in the physicochemical studies of various heterocyclic compounds. For example, one of the methods of calculating the degree of aromaticity of a five-membered heterocycle is to compare the effect of ring current. This can be readily measured by recording the chemical shift values of the proton or carbon in the ring. Not only the δ values of the H or C nuclei but the difference between the δ values corresponding to the α -H and β -H may be used as a criterion of the effect of ring current [1].

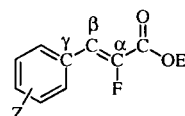
Jones and coworkers examined the chemical shift values of eight *p*-substituted (*p*-Z = H, N(CH₃)₂, OCH₃, CH₃, Cl, Br, CO₂C₂H₅, NO₂) phenylpyrroles (1), 2,5-dimethyl-1-phenylpyrroles, and 3,4-dimethyl-1-phenylpyrroles [2]. They reported a reasonable linear correlation between the chemical shifts of both the α and β protons in pyrroles and Hammett σ_p values for the para substituent but considerably greater deviation from linearity for the α protons. The observed correlation was interpreted in terms of a conjugative interaction of the para substituent with the benzene ring, which is essentially an inductive interaction between the pyrrole nitrogen and aryl substituent. Furthermore, they concluded that there was no appreciable change in ring current.

Correlation of the chemical shift with substituent constant (e.g., Hammett σ) has been widely used to investigate the nature of the effect of the substituent on the physical properties of compounds. Electron density around the nucleus of interest (H, C) is mostly affected by the so-called electron-donating and electron-withdrawing ability of the substituent. Therefore, it seems natural that there should be a correlation between the observed chemical shift and σ . However, other factors such as diamagnetic anisotropy and ring current effect may cause displacement of the signal.

There are quite a few examples of literature reports on the correlation of the chemical shift values with σ . For example, the chemical shift values of the formyl proton of fifteen *m*- and *p*-substituted benzaldehydes in chloroform-*d* and carbon tetrachloride showed a reasonable correlation with σ [3]. Similar correlation of the hydroxyl proton in phenols in dimethyl sulfoxide-*d*₆ was

also reported [4]. For *m*- and *p*-substituted anisoles a reasonably good correlation exists between the methyl resonance and the σ parameter [5].

Robinson, and co-workers, analyzed ^{13}C chemical shift values of substituted ethyl α -fluorocinnamates by applying dual substituent parameter (DSP) and dual substituent parameter-nonlinear resonance (NLR) correlation [6]. They found an excellent correlation for α and γ carbons of the compounds having *p*-substituents. The β and carbonyl carbons showed good correlation for the same series. On the other hand, the correlations for *m*-substituted compounds were generally poorer than those for the *p*-substituted series. It should also be pointed out that α and γ carbons showed a normal substituent effect while β and carbonyl carbons showed an inverse effect.



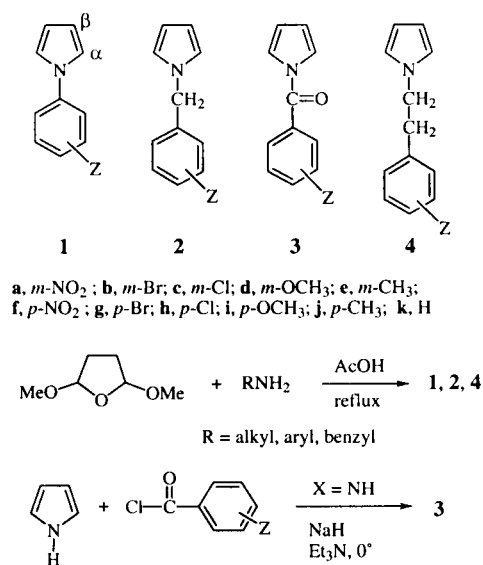
William, *et al.*, reported correlations of chemical shifts versus Hammett σ constants for *p*-substituted phenylhexachlorobicyclo[2.2.1]heptenes and ethylbenzenes [7]. It is worth pointing out that the correlation was best with the β -H which is syn with the 2-phenyl group. In the case of the ethylbenzenes the methyl protons showed better correlation than the methylene protons, although no explanation was given.

Correlation doesn't seem to be limited to the chemical shift and σ . Burke and Frey reported an excellent correlation of *N* chemical shifts in fifteen *N*-alkylnicotinamides and hydride transfer reactivity [8].

The effect of the phenyl ring on the chemical shifts of both the H and C nuclei of the pyrrole ring in substituted pyrroles may give some insight into the nature of the aromaticity of the heterocycles. In the present report we prepared a series of 1-substituted phenyl pyrroles, recorded their nmr spectra, and examined the trends in the chemical shift values.

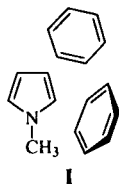
Results and Discussion.

A series of *m*- and *p*-substituted 1-phenyl- (1), 1-benzyl- (2), and 1-(2-phenylethyl)- (4) pyrroles were prepared using a typical procedure of refluxing a mixture of the corresponding 1° amine and 2,5-dimethoxytetrahydrofuran in glacial acetic acid for 1-2 hours [9]. 1-Benzoylpyrroles (3) were prepared by *N*-benzoylation of pyrrole with the corresponding benzoyl chlorides in dichloromethane at 0°. When Friedel-Crafts conditions were employed, the acylation took place at C-2.



The pyrroles were usually purified by distillation under vacuum. Their mp, bp, and yields are listed in Table VIII. All the pyrroles were characterized by nmr (H and C), ir, and mass spectra as well as by elemental analysis; the data are listed in Tables I, II, VIII and IX.

We were interested, first, in the effect of the substituted phenyl group to the chemical shifts of α and β -H and C of the pyrroles. It has been reported that 1-methylpyrrole forms a π -dipole dimer with benzene [10]. A model like I has been suggested. Such model seems to explain the down-field shift of the 1-methyl and α -H signals on dilution in carbon tetrachloride solution, whereas the β -H moves to up-field. Therefore, it was expected that the phenyl group in 1-4 may induce intermolecular association so that the chemical shift should be influenced depending on the nature of association. Therefore, if association occurs, the chemical shifts show a concentration dependence.



The chemical shift values of ^1H and ^{13}C of the pyrroles 1-4 are listed in Tables I and II, respectively. The results of the plotting based on the Tables I and II are shown in Figures 1 and 2 and are listed in Table III. For 1-(2-phenylethyl)pyrroles (4) only seven compounds could be prepared. Therefore, it may be difficult to make a definite argument on the size and sign of the slope of the correlation coefficient for compound 4. However, the trend is quite reasonable; that is, with the exception of the β -H of 4, the β -H's and the β -C's give better correlation with σ than the α -H's and the α -C's.

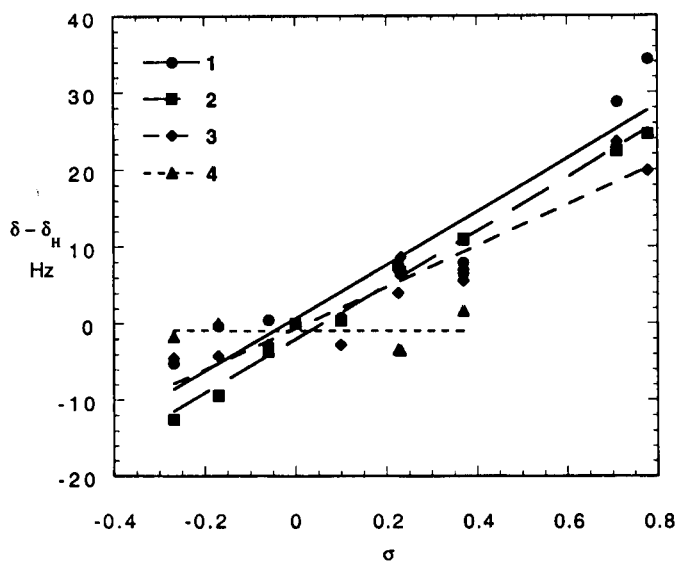


Figure 1. Correlation between σ and ^1H chemical shifts of β -H in 1-4.

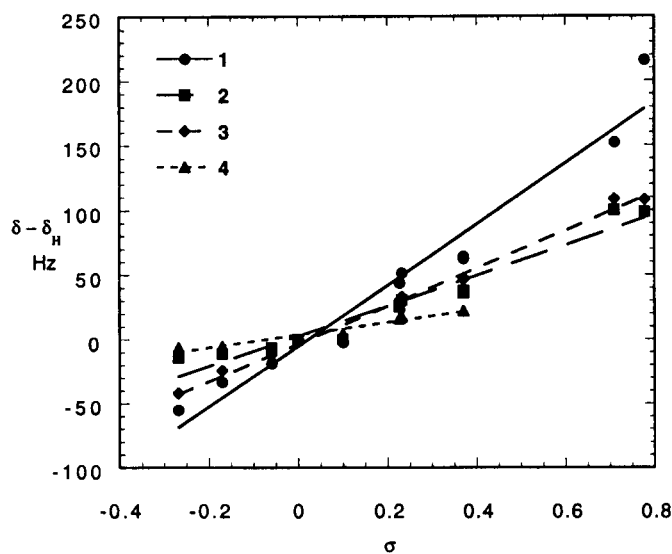


Figure 2. Correlation between σ and ^{13}C chemical shifts of β -C in 1-4.

Table I
¹H NMR Chemical Shift Values (δ) of 1-Substituted Pyrroles in Chloroform-*d*

Compound	2,5	3,4	2'	3'	4'	5'	6'	CH ₂	CH ₂ [a]	CH ₂ [b]
1a	7.17	6.42	8.26		8.09	7.61	7.73			
2a	6.69	6.23	7.98		8.13	7.50	7.36	5.17		
3a	7.25	6.42	8.60		8.47	7.75	8.09			
4a	[c]									
1b	7.07	6.37	7.55		7.36	7.28	7.32			
2b	6.67	6.20	7.23		7.37	7.14	6.98	5.02		
3b	7.26	6.37	7.86		7.64	7.37	7.71			
4b	[c]									
1c	7.08	6.37	7.40		7.21	7.35	7.28			
2c	6.67	6.20	7.06		7.21	7.18	6.93	5.03		
3c	7.26	6.37	7.71		7.54	7.43	7.60			
4c	6.57	6.12	7.09		7.21	7.19	6.93		3.02	4.09
1d	7.10	6.35	6.94		6.79	7.32	6.99			
2d	6.65	6.17	6.62		6.68	7.20	6.78	4.98		
3d	7.27	6.35	7.23		7.06	7.21	7.32			
4d	6.60	6.12	6.56		6.68	7.18	6.76		3.00	4.07
1e	7.09	6.35	7.20		7.03	7.29	7.19			
2e	6.66	6.16	6.92		7.06	7.19	6.90	4.99		
3e	7.29	6.35	7.50		7.29	7.33	7.46			
4e	[c]									
1f	7.19	6.44	7.52	8.32		8.32	7.52			
2f	6.68	6.23	7.19	8.16		8.16	7.19	5.18		
3f	7.23	6.41	7.91	8.37		8.37	7.91			
4f	[c]									
1g	7.06	6.37	7.27	7.54		7.54	7.27			
2g	6.65	6.19	6.92	7.38		7.38	6.92	5.00		
3g	7.27	6.38	7.66	7.62		7.62	7.66			
4g	6.56	6.11	6.92	7.39		7.39	6.92		2.99	4.08
1h	7.06	6.37	7.33	7.39		7.39	7.33			
2h	6.66	6.19	7.12	7.37		7.37	7.12	5.02		
3h	7.26	6.37	7.70	7.49		7.49	7.70			
4h	6.56	6.11	6.97	7.24		7.24	6.97		3.01	4.08
1i	7.01	6.34	6.95	7.31		7.31	6.95			
2i	6.64	6.14	7.04	6.82		6.82	7.04	4.95		
3i	7.30	6.35	7.74	6.96		6.96	7.74			
4i	6.59	6.12	6.99	6.82		6.82	6.99		2.98	4.06
1j	7.07	6.35	7.22	7.28		7.28	7.22			
2j	6.66	6.15	7.09	6.98		6.98	7.09	4.96		
3j	7.30	6.35	7.59	7.22		7.22	7.59			
4j	6.60	6.12	6.99	7.10		7.10	6.99		3.01	4.07
1k	7.09	6.35	7.43	7.39	7.24	7.39	7.43			
2k	6.65	6.17	7.07	7.28	7.22	7.28	7.07	4.99		
3k	7.29	6.36	7.67	7.42	7.53	7.42	7.67			
4k	6.60	6.12	7.10	7.29	7.23	7.29	7.10		3.05	4.10

[a] Phenyl-CH₂. [b] Pyrrolyl-CH₂. [c] Not prepared.

Table II
¹³C NMR Chemical Shift Values (δ) of 1-Substituted Pyrroles in Chloroform-*d*

Compound	2,5	3,4	1'	2'	3'	4'	5'	6'	C=O	CH ₂	CH ₂ [a]	CH ₂ [b]
1a	119.1	111.9	141.5	114.8	149.1	120.0	130.5	125.6				
2a	121.1	109.4	140.5	122.8	148.6	122.8	129.8	132.8		52.5		
3a	121.0	114.2	134.8	124.3	148.0	126.7	129.8	134.9	165.2			
4a	[c]											
1b	118.9	111.0	141.8	123.5	123.6	128.5	130.8	118.9				
2b	120.9	108.8	140.4	130.6	122.7	129.8	130.2	125.4		52.5		
3b	121.0	113.4	135.0	132.1	122.4	134.9	129.9	127.1	165.8			
4b	[c]											
1c	119.2	111.0	141.8	120.6	135.7	125.6	130.6	118.4				
2c	121.0	108.8	140.2	127.7	134.6	127.0	129.9	124.4		52.6		
3c	120.9	113.4	134.4	129.6	132.0	134.4	129.2	127.3	165.8			

Table II (continued)

Compound	2,5	3,4	1'	2'	3'	4'	5'	6'	C=O	CH ₂	CH ₂ [a]	CH ₂ [b]
4c	120.4	108.2	140.3	128.8	134.2	126.9	129.8	126.8			38.0	50.8
1d	119.4	110.3	141.9	106.7	160.4	112.9	130.3	110.8				
2d	121.1	108.4	139.7	112.8	159.9	112.6	129.6	119.1		53.1		
3d	121.1	113.0	134.3	114.3	159.4	118.3	129.4	121.6	167.3			
4d	120.4	107.9	139.9	114.1	160.0	112.0	129.4	120.9			38.3	50.9
1e	119.3	110.1	140.7	131.3	139.5	126.4	129.3	117.6				
2e	121.1	108.4	138.3	128.6	138.8	127.7	128.3	124.1		53.3		
3e	120.9	112.7	132.9	129.7	138.0	132.6	127.9	126.2	167.3			
4e	[c]											
1f	119.1	112.5	144.7	119.4	125.6	145.2	125.6	119.4				
2f	121.2	109.4	147.5	127.4	124.0	145.7	124.0	127.4		52.6		
3f	121.0	114.2	138.8	130.2	123.7	149.7	123.7	130.2	165.6			
4f	[c]											
1g	119.2	110.9	139.8	121.9	132.6	118.9	132.6	121.9				
2g	121.0	108.7	137.2	129.5	131.7	121.4	131.7	129.5		52.5		
3g	121.1	113.4	132.0	131.0	131.8	127.2	131.8	131.0	166.7			
4g	120.4	108.1	137.4	130.4	131.6	120.4	131.6	130.4			37.8	50.8
1h	119.3	110.8	139.0	121.6	129.6	132.0	129.6	121.6				
2h	120.9	108.7	136.6	128.7	128.2	133.3	128.2	128.7		52.4		
3h	121.2	113.4	131.5	130.9	128.8	138.8	128.8	130.9	166.6			
4h	120.4	108.1	136.8	130.0	128.6	132.4	128.6	130.0			37.7	50.9
1i	119.7	109.8	134.5	122.2	114.6	157.6	114.6	122.2				
2i	120.8	108.3	130.1	128.4	114.0	159.0	114.0	128.4		52.7		
3i	121.2	112.6	125.1	131.8	113.7	162.9	113.7	131.8	167.0			
4i	120.5	107.9	130.4	129.6	113.9	158.2	113.9	129.6			37.5	51.4
1j	119.4	110.0	138.4	120.5	130.0	135.3	130.0	120.5				
2j	120.9	108.3	137.2	127.0	129.3	135.1	129.3	127.0		53.0		
3j	121.0	112.7	130.1	129.4	128.9	142.8	128.9	129.4	167.3			
4j	120.5	107.9	136.1	128.5	129.2	135.3	129.2	128.5			37.9	51.3
1k	119.3	110.3	140.7	120.5	129.5	125.6	129.5	120.5				
2k	121.0	108.4	138.1	126.9	128.6	128.5	128.6	126.9		53.2		
3k	120.9	112.9	132.9	129.2	128.2	131.9	128.2	129.2	167.3			
4k	120.4	108.0	138.4	128.5	128.6	126.6	128.6	128.5			38.4	51.1

[a] Phenyl-CH₂. [b] Pyrrolyl-CH₂. [c] Not prepared.

Table III

Slopes (Hz) and Correlation Coefficients (in Parenthesis) of the Plots of ¹H and ¹³C Chemical Shift Values versus σ of 1-4 in Chloroform-*d* (0.1 M)

Compound	2,5(α)-H	3,4(β)-H	2,5(α)-C	3,4(β)-C
1	45.34 (0.779)	34.62 (0.935)	-43.67 (0.876)	237.68 (0.977) [d]
2 [a]	16.77 (0.916)	35.17 (0.995)	21.69 (0.651)	117.90 (0.973)
3 [b]	-25.15 (0.953)	26.88 (0.948)	-33.77 (0.975)	146.16 (0.995)
4 [c]	-22.04 (0.624)	-0.09 (0.010)	-6.08 (0.571)	48.94 (0.970)

[a] ¹H of CH₂: 85.40 (0.942); ¹³C of CH₂: -55.86 (0.599). [b] ¹³C of C=O: -245.22 (0.905). [c] ¹H of phenyl-CH₂: 5.18 (0.157); ¹H of pyrrolyl-CH₂: 10.61 (0.410); ¹³C of phenyl-CH₂: 31.60 (0.210); ¹³C of pyrrolyl-CH₂: -99.00 (0.990). [d] For 1.0 M, 241.07 (0.995); 0.01 M, 235.50 (0.960).

As shown in Figure 1 and Table III, the chemical shift values of the β -H of the 1-benzylpyrroles, (**2**), show excellent correlations ($r = 0.995$) with typical σ values (σ_m and σ_p) in the literature [11]. The α -H's of **2** ($r = 0.916$) and **3** ($r = 0.953$) and the β -H's of **1** ($r = 0.935$) and **3** ($r = 0.948$) show fair correlations with σ . On the other hand, α -H of **1** shows poor correlation ($r = 0.779$). Furthermore, 1-(2-phenylethyl)pyrroles (**4**) show no correlation regardless of α -H or β -H. Although the β -H of **2** shows the best correlation coefficient, the magnitude of the slope ($\rho = 35.17$ Hz) was very close to that of the β -H of **1** ($\rho = 34.62$ Hz). The

magnitude of the slope of the β -H of **3** is the smallest ($\rho = 26.88$ Hz) among **1**, **2**, and **3**.

Although the correlations to σ are poor with α -H's, the relative magnitudes of the slopes and their signs are quite contrasting. The signs of the slopes of **1** and **2** are positive whereas they are negative for **3** and **4**. The absolute magnitude of the slope of **1** is the largest among the four series. The signs of the slopes of the α -H and β -H of **3** are opposite although their absolute magnitude and the correlation coefficients are very close: -25.15 Hz ($r = 0.953$) and +26.88 Hz ($r = 0.948$) for α -H and β -H, respectively.

The observation seems unusual because the magnitude of the slope in a Hammett plot is generally affected by the distance from the substituent if through-bond transmission is the major effect of the substituent. In the case of **4** the pyrrolyl and the phenyl rings are separated by $-\text{CH}_2\text{CH}_2-$ and the transmission of the effect of the substituent through bonds should be almost negligible, as is reflected the lack of a correlation of $\beta\text{-H}$ in **4** ($r = 0.010$). But the distance seems not to be the sole influencing factor on the effect of the substituent. The phenyl ring is directly attached to the pyrrole ring in **1**, whereas it is separated by CH_2 and $\text{C}=\text{O}$ in **2** and **3**, respectively. Therefore, one would expect the largest value of slope would be for $\alpha\text{-H}$ of **1** or CH_2 of **2**, which is not the case. If transmission of the effect through bonds is the major factor, one would also expect very similar slope and correlation coefficients for the chemical shifts of CH_2 in **2** and **4**. However, the magnitudes of the slopes (85.40 Hz for **2** and 5.18 Hz for **4**) and the correlation coefficients (0.942 for **2** and 0.157 for **4**) are not close at all. Furthermore, the $\beta\text{-H}$ of **3** should also show similar correlation to that of **2** because their distances from the phenyl ring are similar. However, their slopes and correlation coefficients are fairly different.

Correlation between the chemical shifts of the $\beta\text{-carbon}$ and σ is more remarkable than that of the $\beta\text{-proton}$ as shown in Figure 2. At first, we plotted the ^{13}C chemical shift values of the pyrrole carbon against the $^{13}\sigma$ substituent constant proposed by Taft [12]; the results are listed in Table IV. As shown in Table IV the correlations are generally poor for the $\alpha\text{-C}$ but a little better for the $\beta\text{-C}$. Then we used σ_m and σ_p values [11] for similar plotting and tabulated the slopes and correlation coefficients in Table III. Although the trends in Tables III and IV are very similar, it is clearly noticeable that the correlation coefficients are poorer for $\alpha\text{-C}$ for each series than when the $^{13}\sigma$ values are used, but they are much better for the $\beta\text{-C}$.

Taft's $^{13}\sigma$ values in the literature [12] originated from the $\beta\text{-C}$ chemical shift values of substituted styrenes. The $\beta\text{-C}$ of styrene can be considered as the terminus of conjugation of the conjugated system and the substituent effect may be transmitted through conjugation as follows:

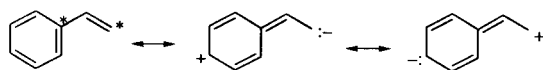


Table IV

Slopes (Hz) and Correlation Coefficients (in Parenthesis) of the Plots of ^{13}C Chemical Shift Values versus $^{13}\sigma$ of **1-4** in Chloroform-*d* (0.1 M)

Compound	2,5(α)-C	3,4(β)-C	CH_2 or CO
1	-32.79 (0.933)	160.84 (0.943)	
2	18.59 (0.780)	77.45 (0.911)	-26.28 (0.394)
3	-22.65 (0.927)	98.86 (0.925)	-146.60 (0.767)
4	-3.39 (0.649)	27.22 (0.856)	43.80 (0.460) [a], -58.98 (0.930) [b]

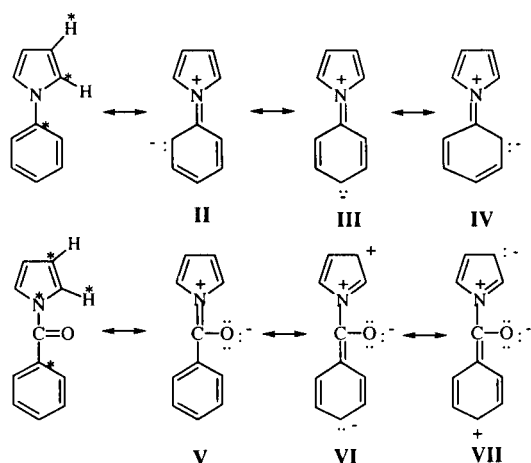
[a] ^{13}C of phenyl- CH_2 . [b] ^{13}C of pyrrolyl- CH_2 .

Therefore, it may not be proper to apply $^{13}\sigma$ values derived from the styrenes to the pyrrole derivatives. Application of dual substituent parameter values (σ_1 and σ_{R^0}) [13] also did not give a meaningful correlation between δ_{obs} and δ_{calcd} .

Table III shows several interesting phenomena. First, neither the methylene carbons of **2** nor the carbonyl carbons of **3** show correlation with σ . These carbons also show no correlation with $^{13}\sigma$ as shown in Table IV. They are directly bonded to the benzene ring and at least a fair correlation is expected. Secondly, the signs of the slopes for the $\beta\text{-H}$ and the $\beta\text{-C}$ of **1-3** are positive indicating normal substituent effect whereas they are positive for $\alpha\text{-H}$ and $\alpha\text{-C}$ of **2** and $\alpha\text{-H}$ of **1** but negative for $\alpha\text{-H}$ and $\alpha\text{-C}$ of **3** and $\alpha\text{-C}$ of **1**. Although the magnitudes of the correlation coefficients are too different to give a meaningful consideration, the trends are quite clear and there are inverse effects for the series of $\alpha\text{-H}$ and $\alpha\text{-C}$ of **3** and $\alpha\text{-C}$ of **1**. Thirdly, the value of the slope of the plot of $\beta\text{-C}$, which shows the best correlation coefficients ($r = 0.970-0.995$) among all the series show the order of **1** > **3** > **2** > **4**. The smallest slope of **4** which is about one fourth of that of **1** can be readily understood by the longest distance of the $\alpha\text{-C}$ of **4** from the substituent. Fourthly, the ^1H chemical shifts of both methylenes in **4** show no correlation at all, but ^{13}C of pyrrolyl- CH_2 in the same series show an excellent correlation ($r = 0.990$) with a negative slope of substantial magnitude (-99 Hz). This is in contrast to the positive slope of the correlation of the proton signal of the methyl group in ethylbenzene with σ [7]. On the other hand, the ^{13}C of phenyl- CH_2 in **4** shows no correlation ($r = 0.210$).

It seems apparent that our observations cannot be explained by analogy to the literature rationale. For example, we may apply the phenomenon of better correlation of alternating carbons [8] in the case of **3** because the conjugation of the two rings is possible as illustrated by resonance structures **V-VII**. The best correlation observed with the $\beta\text{-C}$ of **3** may be explained as such. The $\alpha\text{-H}$ of **3** should also show good correlation using the same logic. However the observed correlation coefficient is not as good as that of the $\beta\text{-C}$. Furthermore, the signs of the slopes which are + for the $\beta\text{-C}$ and - for the $\alpha\text{-H}$ are not consistent with the concept of the alternating atoms. A similar argument should give a better correlation with $\alpha\text{-C}$, not $\beta\text{-C}$, of **1**, which may be considered as a resonance hybrid of **II-IV**, but the observation is the opposite.

If the changes in chemical shift are primarily due to the effect of electron density, then good correlation can be expected in the plot of δ_{H} against δ_{C} for each position of α or β . The results of such plots are listed in Table V, which show good correlation with the β positions of **1**, **2**, and **3** but poor correlation with the α positions of the series. The



correlation of the α position of **3** may be considered fair but the slope is about one fourth of that of the β . The close values of the slope and the correlation coefficient for the β s of **1** (6.37, $r = 0.975$) and **3** (5.03, $r = 0.971$) may be considered only as an indication that a very similar mechanism of the transmission of the effect of the substituent operates in these series.

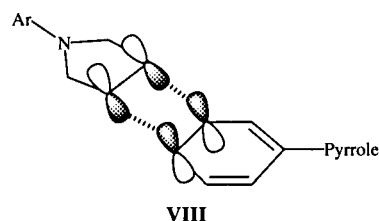
Table V

Slopes (Hz) and Correlation Coefficients (in Parenthesis) of the Plots of the Chemical Shift Values of ^1H versus ^{13}C of the 1-Substituted Pyrroles

Series	2,5(α)	3,4(β)
1	-0.61 (0.713)	6.37 (0.975)
2	1.12 (0.618)	3.29 (0.961)
3	1.23 (0.938)	5.03 (0.971)
4	0.16 (0.691)	-0.91 (0.159)

Our observations seem to be consistent with through-space transmission of the effect of the substituent which is possible by a stacking conformation as shown in **VIII**. If intermolecular stacking takes place, it may be between the p orbitals of the β -Cs of a pyrrole ring and the p orbitals of m - and p -C of a phenyl ring. This model may explain the most effective transmission of the substituent

effect to the β -C, which then results in the best correlation of the chemical shift with the σ .



The possibility of stacking is supported by a linear dependence of chemical shift on the concentration. The ^1H chemical shift values of the unsubstituted phenyl pyrroles (**1k**, **2k**, **3k**, and **4k**) show excellent linearities ($r = 0.997$ - 0.999) with the concentration as shown in Figure 3. The values are shifted upfield as the concentration increases. Similar plotting of the ^{13}C chemical shift values also show excellent linearities (not shown). Table VI lists the slopes

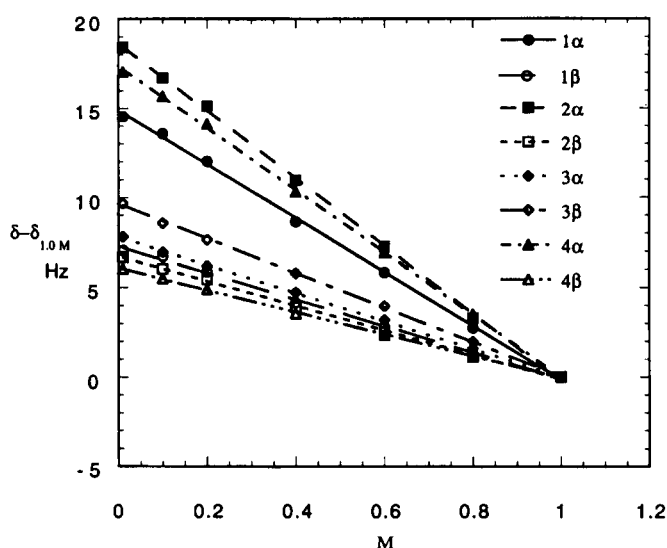


Figure 3. Correlation between the concentration and the difference in the ^1H chemical shift values (1.0 M as reference) of α - and β -H of the unsubstituted phenyl derivatives of the pyrroles (**1k**, **2k**, **3k**, and **4k**).

Table VI

Slopes (Hz) [a] and Intercepts (in Parenthesis) of the Plots of ^1H and ^{13}C Chemical Shift Values versus Concentrations of the Unsubstituted Phenyl Derivatives of the Pyrroles

Compound	2,5(α)-H	3,4(β)-H	2,5(α)-C	3,4(β)-C
1k	15 ± 0.5 (14.86)	7 ± 0.3 (7.27)	10 ± 0.3 (10.11)	1 ± 0.2 (0.96)
2k [b]	19 ± 0.5 (18.63)	7 ± 0.3 (6.72)	11 ± 0.3 (11.26)	6 ± 0.3 (5.94)
3k [c]	8 ± 0.3 (7.81)	9 ± 0.3 (9.63)	15 ± 0.3 (15.74)	12 ± 0.3 (11.84)
4k [d]	17 ± 0.5 (17.36)	6 ± 0.2 (6.09)	12 ± 0.3 (12.00)	7 ± 0.2 (7.38)

[a] All the slopes are negative values indicating the chemical shift values move upfield as the concentration increases. [b] ^1H of CH_2 : 33 ± 0.2 (32.86); ^{13}C of CH_2 : 17 ± 0.2 (16.43). [c] ^{13}C of $\text{C}=\text{O}$: 19 ± 0.2 (19.27). [d] ^1H of phenyl- CH_2 : 25 ± 0.2 (25.55); ^1H of pyrrolyl- CH_2 : 22 ± 0.2 (21.97); ^{13}C of phenyl- CH_2 : 13 ± 0.2 (12.99); ^{13}C of pyrrolyl- CH_2 : 16 ± 0.2 (15.95).

and intercepts of the plots of $\Delta\delta$ (in Hz) against the concentration (0.01-1.0 M). The magnitude of the slope of the α -Hs of **1k**, **2k**, and **4k** is about 2-3 times greater than those of the β -Hs. But the slope of the α -H of **3k** is a little smaller than that of the β -H.

In order to examine the effect of concentration on the linearity of the plot of the chemical shifts of **1** vs the Hammett σ , the spectra of **1** (except **1a** and **1f** due to solubility) were obtained at concentrations of 1.0 M, 0.1 M, and 0.01 M in chloroform-*d*. The most concentrated solution (1.0 M) showed an excellent linearity ($r = 0.995$) with β -C. On the other hand, the correlation was fair when the data of 0.01 M solution were used ($r = 0.960$). This observation provides an additional evidence for stacking of **1** in solution.

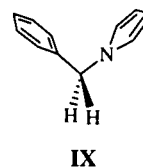
We also examined the effect of 1-pyrrolyl, 1-pyrrolylmethyl, and 1-pyrroloyl groups on the chemical shifts of protons and carbons in the benzene ring. There is ample literature data on the effects of substituents on the benzene ring [14]. However, to our knowledge a systematic study on the effect of pyrrole as substituent has not been reported.

One would expect a similar effect between pyrrolyl and phenyl group on the chemical shift of the *ortho*-H of benzene ring if the former exerts a comparative magnitude of ring current as the latter. On the other hand, the electronic effect of the N atom which is directly bonded to the benzene ring may be the predominant one and, if this is the case, the chemical shift values may show an unusual trend. As shown in Table VII, the electron-donating nature of the nitrogen atom through resonance such as **II-IV** seems to be predominant and the chemical shift values on the *o*-, *m*-, and *p*-H in the phenyl ring are shifted up-field by $\Delta\delta$ 0.21, 0.07, and 0.15, respectively relative to those in biphenyl.

Contrary to the case of 1-pyrrolyl and phenyl, the effect of 1-pyrroloyl and benzoyl are essentially similar, showing $\Delta\delta$ of 0.02-0.04. Apparently, the diamagnetic anisotropic effect of the carbonyl group seems to be the predominant factor to influence the chemical shift of protons in benzene ring.

In the case of 1-pyrrolylmethyl the inductive effect of the nitrogen atom should cause down-field shift of the protons in the benzene compared to those of toluene and ethylbenzene. This seems to be the case with the *m*- and *p*-H, but the *o*-H signal is shifted upfield compared to that of ethylbenzene. Molecular modeling with HyperChem software reveals that

the most stable conformation of **2** is with the planes of the pyrrole and the benzene form a V-shape as shown in **IX**. Therefore, the *ortho*-H may be shielded by the ring current of the pyrrole ring.



The effect of the 1-pyrrolyl group on the ^{13}C chemical shift of the benzene ring seems to be similar to that of phenyl, but the magnitude is variable as shown in Table VII. The resonance contribution of the lone-pair electrons on the nitrogen atom allows the *ortho* and the *para* carbons to bear a negative charge as shown in **II-IV**, causing a significant up-field shift as in the proton case. For 1-pyrroloyl the resonance contribution of forms such as **V** and **VI** make the carbonyl group less electron-withdrawing and the *ipso*-C signal is shifted only 4.6 ppm whereas a benzoyl group causes a down-field shift of 9.3 ppm (Table VII).

In summary, synthesis and spectral studies of a series of 1-phenyl, 1-benzyl-, and 1-benzoylpyrroles is reported. Evidence is presented for an intermolecular stacking interaction between molecules of 1-phenylpyrrole in solution. The evidence includes the linear concentration dependence of the chemical shifts and the better correlation of the β proton and carbon chemical shifts with Hammett σ than the α proton and carbon chemical shifts. In addition, the substituent effect of the 1-pyrrolyl, 1-pyrrolylmethyl, and 1-pyrroloyl groups on the chemical shifts of protons and carbons in an attached phenyl group are reported.

EXPERIMENTAL

Melting points were determined on a Fischer MEL-TEMP apparatus and are uncorrected. Semiempirical molecular orbital calculations (AM1) were performed on a personal computer with HyperChem software. Nuclear magnetic resonance (nmr) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University with chloroform-*d* as the solvent at 400 MHz for ^1H and 100 MHz for ^{13}C and were referenced to tetramethylsilane. The concentration of the solution was

Table VII

Substituent Constants of 1-Pyrrolyl, 1-Pyrrolylmethyl, and 1-Pyrroloyl Groups for the ^1H and ^{13}C Chemical Shifts (in ppm) of Phenyl Ring

Substituent	<i>ortho</i> -H	<i>meta</i> -H	<i>para</i> -H	<i>ipso</i> -C	<i>ortho</i> -C	<i>meta</i> -C	<i>para</i> -C
1-Pyrrolyl	0.16	0.13	-0.05	12.2	-8.2	0.9	-2.9
1-Pyrrolylmethyl	-0.18	-0.01	-0.06	10.5	-1.4	0.3	-1.5
1-Pyrroloyl	0.45	0.17	0.24	4.6	0.8	-2.2	3.6
COC_6H_5 [a, b]	0.47	0.13	0.22	9.3	1.6	-0.3	3.7
Phenyl [a, b]	0.37	0.20	0.10	13.1	-1.1	0.5	-1.1
CH_3 [a, b]	-0.20	-0.02	-0.22	9.2	0.7	-0.1	-3.0
CH_2CH_3 [a, b]	-0.14	-0.06	-0.07	15.7	-0.6	-0.1	-2.8

[a] For ^1H , from reference 14, p. H255 and H295. [b] For ^{13}C , from reference 14, p. C120.

Table VIII
Yields, Boiling or Melting Points, and Analytical Data of 1-Arylpyrroles

	[a] %	mp, bp °C (mm)	Formula (M.W.)	Calcd., %			Found., %		
				C	H	N	C	H	N
1a	47	72-74	C ₁₀ H ₈ N ₂ O ₂ (188.19)	63.82	4.29	14.89	63.71	4.44	15.02
2a	61	131 (0.003)	C ₁₁ H ₁₀ N ₂ O ₂ (202.21)	65.34	4.99	13.85	65.19	5.06	14.00
3a	61	131 (0.01)	C ₁₁ H ₈ N ₂ O ₃ (216.20)	61.11	3.73	12.96	61.22	4.04	13.16
1b	30	62-64	C ₁₀ H ₈ BrN (222.08)	54.08	3.63	6.31	54.32	3.88	6.12
2b	53	81 (0.03)	C ₁₁ H ₁₀ BrN (236.12)	55.96	4.27	5.93	56.14	4.40	6.14
3b	67	98 (0.008)	C ₁₁ H ₈ BrNO (250.10)	52.83	3.22	5.60	52.86	3.18	5.59
1c	23	50-51	C ₁₀ H ₈ ClN (177.63)	67.62	4.54	7.88	67.45	4.34	7.60
2c	53	69 (0.006)	C ₁₁ H ₁₀ ClN (191.66)	68.94	5.26	7.31	69.17	5.37	7.54
3c	21	84 (0.025)	C ₁₁ H ₈ ClNO (205.64)	64.25	3.92	6.81	64.61	4.26	6.56
4c	50	[b]	C ₁₂ H ₁₂ ClN (205.68)	70.07	5.88	6.81	70.25	5.64	6.95
1d	51	[b]	C ₁₁ H ₁₁ NO (173.22)	76.27	6.40	8.09	76.53	6.19	8.28
2d	25	81 (0.007)	C ₁₂ H ₁₃ NO (187.24)	76.98	6.99	7.48	77.12	7.16	7.64
3d	30	116 (0.04)	C ₁₂ H ₁₁ NO ₂ (201.23)	71.63	5.51	6.96	71.46	5.64	6.85
4d	67	[b]	C ₁₃ H ₁₅ NO (201.27)	77.58	7.51	6.96	77.39	7.48	6.80
1e	23	[b]	C ₁₁ H ₁₁ N (157.22)	84.04	7.05	8.91	84.33	7.15	8.82
2e	13	91 (0.24)	C ₁₂ H ₁₃ N (171.24)	84.12	7.66	8.22	83.99	7.43	8.55
3e	43	83 (0.1)	C ₁₂ H ₁₁ NO (185.23)	77.81	5.99	7.56	76.27	5.18	6.40
1f	48	178-180	C ₁₀ H ₈ N ₂ O ₂ (188.19)	63.82	4.29	14.89	63.59	4.34	14.95
2f	43	105 (0.12)	C ₁₁ H ₁₀ N ₂ O ₂ (202.21)	65.34	4.99	13.85	65.12	4.85	13.66
3f	61	114-118	C ₁₁ H ₈ N ₂ O ₃ (216.20)	61.11	3.73	12.96	61.36	4.03	13.05
1g	37	95-96	C ₁₀ H ₈ BrN (222.08)	54.08	3.63	6.31	54.33	3.75	6.02
2g	46	84 (0.03)	C ₁₁ H ₁₀ BrN (236.12)	55.96	4.27	5.93	55.80	4.41	5.70
3g	41	95 (0.06)	C ₁₁ H ₈ BrNO (250.10)	52.83	3.22	5.60	53.07	3.25	5.58
4g	64	[b]	C ₁₂ H ₁₂ BrN (250.13)	57.61	4.83	5.60	57.84	4.65	5.46
1h	50	81-82	C ₁₀ H ₈ ClN (177.63)	67.62	4.54	7.88	67.50	4.44	7.64
2h	59	69 (0.02)	C ₁₁ H ₁₀ ClN (191.66)	68.94	5.26	7.31	68.78	5.09	7.31
3h	34	92-93 (0.025)	C ₁₁ H ₈ ClNO (205.64)	64.25	3.92	6.81	64.16	3.88	6.92
4h	50	[b]	C ₁₂ H ₁₂ ClN (205.68)	70.07	5.88	6.81	70.19	5.58	6.97
1i	16	104-108	C ₁₁ H ₁₁ NO (173.22)	76.27	6.40	8.09	76.01	6.38	7.82
2i	37	82-83 (0.0045)	C ₁₂ H ₁₃ NO (187.24)	76.98	6.99	7.48	76.87	7.11	7.25
3i	36	114 (0.01)	C ₁₂ H ₁₁ NO ₂ (201.23)	71.63	5.51	6.96	71.66	5.67	6.70
4i	28	[b]	C ₁₃ H ₁₅ NO (201.27)	77.58	7.51	6.96	77.25	7.36	6.97
1j	69	80-82	C ₁₁ H ₁₁ N (157.22)	84.04	7.05	8.91	84.21	7.23	8.67
2j	14	87 (0.25)	C ₁₂ H ₁₃ N (171.24)	84.12	7.66	8.22	84.24	7.80	7.96
3j	35	85-88 (0.02)	C ₁₂ H ₁₁ NO (185.23)	77.81	5.99	7.56	78.00	6.08	7.52
4j	65	[b]	C ₁₃ H ₁₅ N (185.27)	84.28	8.16	7.56	84.52	8.35	7.29
1k	28	59-60	C ₁₀ H ₉ N (143.19)	83.88	6.34	9.78	83.67	6.15	10.10
2k	26	58-59 (0.04)	C ₁₁ H ₁₁ N (157.22)	84.03	7.06	8.91	84.14	7.24	8.70
3k	62	74 (0.02)	C ₁₁ H ₉ NO (171.20)	77.17	6.48	7.99	77.23	6.46	8.18
4k	33	[b]	C ₁₂ H ₁₃ N (171.24)	84.17	7.65	8.18	84.35	7.68	7.95

[a] Yield. [b] Viscous liquid.

0.10 M unless otherwise noted. Infrared (ir) spectra were recorded on a JASCO Model IR Report-100 spectrophotometer as potassium bromide pellets or neat. Electron-impact mass spectra (ms) were obtained using a JEOL JMS-AX505WA mass spectrometer in the Research Center for New-Biomaterials in Agriculture, Seoul National University, Suwon. Elemental analyses were performed by the M-H-W Laboratories, Phoenix, Arizona.

An Illustrative Procedure for 1-Phenylpyrroles (1), 1-Benzylpyrroles (2), and 1-(2-Phenylethyl)pyrroles (4).

A mixture of benzylamine (45 mmoles), 2,5-dimethoxytetrahydrofuran (60 mmoles), and glacial acetic acid (30 ml) was refluxed for 2 hours. After cooling to room temperature, the mixture was poured into water (300 ml) and extracted with diethyl ether (4 x 100 ml). The organic extract was washed with saturated

sodium bicarbonate solution and dried. The final product was isolated using vacuum distillation.

An Illustrative Procedure for 1-Benzoylpyrroles (3).

Sodium hydride (105 mmoles, pretreated with hexane) was suspended in tetrahydrofuran (40 ml). Pyrrole (52 mmoles) was added and the mixture was stirred for a few min until the evolution of gas stopped. Benzoyl chloride (35 mmoles) was added dropwise for 1 hour. The mixture was mixed with water (200 ml) and extracted with diethyl ether. Final purification was performed by vacuum distillation.

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Table IX
Infrared and Electron Impact (EI)-Mass Spectral Data of 1-Arylpyrroles

	Ir, cm ⁻¹	Mass, m/z (%)
1a	[a] 1535 s, 1520 s, 1350 s, 1315 m, 1250 m, 1050 w, 1010 w, 925 w, 860 w, 790 w, 730 vs	189 (12), 188 (100), 142 (50), 141 (28), 115 (27), 58 (18)
2a	[b] 1520 vs, 1485 s, 1430 s, 1340 vs, 1280 s, 1070 s, 1050 s, 800 s, 715 vs	202 (100), 136 (82), 90 (42)
3a	[b] 1690 vs, 1530 s, 1460 m, 1335 vs, 1080 s, 1060s, 900 s, 840 m, 745 s, 715 s	216 (35), 150 (100), 104 (40), 97 (49)
1b	[a] 1585 s, 1565 s, 1495 s, 1425 m, 1335 m, 1310 m, 1055 s, 1050 s, 775 s, 735 vs	223 (66), 221 (68), 142 (22), 119 (24), 115 (38), 71 (12), 58 (100)
2b	[b] 1585 m, 1560 m, 1490 ms, 1420 ms, 1290 ms, 1070 s, 1050 s, 770 m, 720 s	235 (75), 169 (100), 90 (39)
3b	[b] 1690 vs, 1560 m, 1460 s, 1410 s, 1400 s, 1330 vs, 1300 s, 1075 vs, 1060 s, 890 s, 800 m, 740 s, 715 s	249 (36), 183 (100), 155 (35), 76 (22)
1c	[a] 1595 s, 1575 s, 1500 vs, 1470 m, 1435 m, 1335 m, 1315 m, 1155 m, 1085 m, 1060 s, 1050 s, 1010 m, 860 m, 780 s, 730 vs	179 (5), 177 (14), 149 (3), 142 (3), 119 (7), 105 (3), 58 (100)
2c	[b] 1590 s, 1570 s, 1490 s, 1470 s, 1430 s, 1280 s, 1070 s, 1050 s, 770 s, 720 s	191 (100), 125 (100), 89 (23)
3c	[b] 1685 vs, 1580 w, 1565 m, 1455 s, 1410 s, 1395 s, 1320 vs, 1295 s, 1075 s, 1055 s, 880 s, 795 m, 760 m 725 vs	205 (54), 139 (100), 111 (37), 94 (31)
4c	[b] 1490 ms, 1470 ms, 1430 ms, 1350 ms, 1275 s, 180 m, 11075 s, 1000 s, 950 ms, 860 m, 775 s, 720 s	207 (18), 205 (45), 197 (6), 180 (6), 140 (12), 139 (16), 138 (31), 130 (74), 103 (20), 80 (100), 58 (19)
1d	[b] 1595 s, 1495 s, 1475 m, 1325 m, 1280 m, 1235 ms, 1230 ms, 1050 m, 1035 m, 820 m, 760 m, 720 s, 680 m	174 (54), 173 (100), 172 (21), 158 (21), 144 (52), 130 (77), 123 (31), 115 (19), 103 (26), 86 (26), 77 (27), 187 (100), 121 (100), 91 (40)
2d	[b] 1590 s, 1580 s, 1480 s, 1430 s, 1280 vs, 1260 vs, 1070 s, 1050 s, 1030 s, 770 m, 720 vs	
3d	[b] 1685 s, 1590 m, 1570 m, 1470 m, 1455 s, 1410 m, 1320 s, 1290 s, 1060 m, 780 m, 735 ms	201 (57), 135 (100), 107 (24), 94 (11)
4d	[b] 2890 s, 2800 m, 1590 s, 1570 s, 1475 s, 1450 s, 1440 s, 1425 s, 1275 s, 1250 s, 1125 ms, 1065 m, 1030 m, 770 m, 720 s, 690 m	201 (40), 200 (9), 134 (28), 130 (96), 1212 (7), 91 (13), 80 (100), 58 (49)
1e	[b] 1595 m, 1575 m, 1490 s, 1465 mw, 1330 m, 1310 mw, 1050 m, 770 m, 710 m, 680 m	157 (39), 156 (13), 149 (24), 107 (36), 106 (16), 58 (100)
2e	[b] 2880 ms, 2830 m, 1600 s, 1490 s, 1440 s, 1340 s, 1280 vs, 1070 s, 1050 s, 770 s, 720 vs	171 (37), 105 (100)
3e	[b] 1685 vs, 1595 m, 1570 m, 1460 s, 1320 vs, 1300 s, 1065 s, 1055 s, 900 m, 780 m, 725 vs	185 (43), 119 (100), 91 (43)
1f	[a] 1580 s, 1510 s, 1500 vs, 1460 s, 1310 vs, 1170 m, 1080 s, 1035 s, 990 m, 830 s, 730 vs	189 (18), 188 (100), 142 (50), 141 (35), 116 (11), 115 (33), 58 (26)
2f	[b] 1600 ms, 1510 s, 1500 s, 1340 vs, 1295 m, 1090 ms, 1085 ms, 790 ms, 725 vs	202 (100), 136 (28), 90 (15)
3f	[a] 1680 s, 1580 m, 1500 s, 1460 s, 1400 s, 1330 vs, 1060 m, 830 s, 730 s, 720 s, 705 s	216 (60), 150 (100), 104 (43), 92 (20)
1g	[a] 1580 m, 1490 vs, 1405 vw, 1100 m, 1050 m, 905 m, 810 m, 720 ms	223 (9), 221 (9), 149 (4), 119 (21), 105 (11), 91 (8), 71 (9), 58 (100)
2g	[b] 1495 s, 1485 s, 1435 s, 1295 s, 1280 s, 1070 s, 1050 s, 795 ms, 720 ms	235 (53), 169 (100), 90 (22)
3g	[b] 1665 s, 1575 m, 1460 m, 1335 ms, 1080 m, 1050 m, 860 w, 820 m, 740 m, 720 m	251 (26), 249 (26), 183 (100), 155 (29), 97 (18)
4g	[b] 1600 m, 1485 ms, 1410 m, 1380 m, 1250 m, 1125 m, 1030 m, 830 m, 770 ms	251 (18), 249 (19), 184 (5), 182 (6), 130 (6), 80 (100), 58 (45)
1h	[a] 1590 m, 1500 vs, 1340 vs, 1105 s, 1080 s, 1060 s, 1000 m, 915 s, 895 vs, 810 s, 730 vs	179 (39), 177 (100), 149 (6), 142 (16), 115 (57), 75 (8), 58 (14)
2h	[b] 1590 w, 1480 s, 1430 ms, 1410 ms, 1280 s, 1070 s, 1050 s, 800 s, 720 s	191 (100), 125 (100), 89 (19)
3h	[b] 1670 s, 1580 m, 1475 m, 1460 ms, 1390 ms, 1330 s, 1070 s, 830 s, 750 s, 730 s	205 (55), 139 (100), 111 (73), 75 (28)
4h	[b] 1490 s, 1280 m, 1225 m, 1075 s, 1000 s, 950 ms, 860 m, 775 s, 720 s	207 (12), 205 (33), 149 (10), 138 (14), 103 (9), 80 (100), 58 (37)
1i	[a] 1510 vs, 1330 m, 1290 m, 1285 m, 1250 s, 1240 s, 1150 m, 1000 ms, 810 s, 710 s	173 (22), 158 (21), 130 (4), 119 (4), 77 (2), 58 (100)
2i	[b] 1605 ms, 1510 s, 1495 ms, 1280 ms, 1240 s, 1160 s, 1070 m, 1020 m, 810 m, 720 m	187 (100), 121 (100), 91 (12)
3i	[b] 1670 vs, 1585 s, 1500 s, 1450 s, 1410 s, 1320 vs, 1255 vs, 1145 s, 865 s, 825 s, 730 s	201 (28), 135 (100), 77 (11)
4i	[b] 1610 ms, 1515 s, 1500 s, 1460 s, 1360 m, 1300 m, 1285 ms, 1250 vs, 1160 m, 1075 m, 1020 m, 820 ms, 720 m	201 (43), 149 (11), 134 (31), 130 (44), 121 (100), 91 (20), 80 (67), 58 (13)
1j	[a] 1520 s, 1470 m, 1320 s, 1110 m, 1060 m, 1000 m, 910 m, 810 s, 710 s	157 (59), 156 (33), 149 (7), 129 (10), 119 (10), 115 (9), 58 (100)

Table IX (continued)

	Ir, cm ⁻¹	Mass, m/z (%)
2j	[b] 1520 s, 1490 s, 1435 s, 1290 s, 1285 s, 1075 s, 1055 s, 800 ms, 720 vs	171 (100), 105 (100)
3j	[b] 1690 s, 1610 ms, 1460 s, 1395 ms, 1330 vs, 1300 s, 1160 m, 1075 s, 1060 s, 875 s, 825 m, 785 m, 730 s	185 (65), 119 (100), 91 (59)
4j	[b] 1605 m, 1580 ms, 1525 s, 1460 ms, 1350 m, 1285 m, 1160 m, 1030 ms, 820 s, 770 ms	186 (6), 185 (38), 130 (24), 118 (35), 105 (22), 80 (77), 58 (100)
1k	[a] 1595 ms, 1580 m, 1500 s, 1450 m, 1310 s, 1245 w, 1160 m, 1050 m, 750 s, 710 vs	144 (12), 143 (100), 116 (23), 115 (42), 104 (5), 77 (10), 58 (95)
2k	[b] 1490 s, 1450 s, 1430 ms, 1280 s, 1070 s, 1050 s, 710 s	157 (100), 91 (100)
3k	[b] 1685 vs, 1470 s, 1450 s, 1405 s, 1335 vs, 1310 s, 1080 s, 1060 s, 880 s, 750 s, 730 s, 700 s	171 (39), 105 (100), 77 (30)
4k	[b] 1495 s, 1450 m, 1360 m, 1285 s, 1075 m, 1055 m, 720 s, 695 s	172 (8), 171 (59), 130 (62), 104 (30), 80 (100), 58 (45)

[a] Potassium bromide pellet. [b] Neat.

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