a desiccator. For each run the KSCN was weighed, added to the dried fused acetate melt in the reaction vessel, stirred until dissolved, and vacuum dried at 200 °C for 1 h. **1** was added to the reaction vessel and the reaction followed in the normal way.

Stability of KSCN in Fused Acetate Melt. KSCN (0.321 g, 3.31 mmol) and 4.03 g (48.6 mmol) of fused acetate melt were mixed in a test tube and heated for 2.5 h at 200 °C. The physical appearance changed from clear to very light yellow. The mixture was dissolved in water and the amount of KSCN was found to be 0.320 g (3.29 mmol) by the Volhard method. This represents only a 0.5% loss of KSCN.

Density of Melts at 200 °C. A 25-mL volumetric flask was weighed, filled with dried molten KSCN at 200 °C, and reweighed. The density of KSCN at 200 °C is 1.59 g/mL; of the acetate eutectic, 1.39 g/mL.

References and Notes

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Patterns of Carbon-13 Chemical Shift Response to Substituent Effects in Arylcarbenium Ions. The 2-Furyl, 2-Thienyl, 2-Benzofuryl, and 2-Benzothienyl Systems[1]

David A. Forsyth*[2a] and George A. Olah*[2b]

Contribution from the Department of Chemistry, Clarkson College of Technology,
Potsdam, New York 13676, and the Department of Chemistry,
University of Southern California, Los Angeles, California 90007.

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Abstract: The response of ^{13}C chemical shifts at the ring positions in arylcarbenium ions to changes in substituents at the carbenium center is examined by plotting the chemical shifts vs. the chemical shifts at the para position in phenylcarbenium ions. In a previous study of hydrocarbon arylcarbenium ions, the slope of the response for a particular position was shown to be related to the amount of positive charge developed at that position. For heteroarylcarbenium ions, linear responses are also found, and these appear to at least qualitatively reflect the charge distribution patterns in the cations. However, the correlation of response slopes with calculated charge densities exhibits some obviously deviant points. The unusually high sensitivity of the C_5 position in thiophene is discussed in relation to calculated charges, nonadditivity of substituent chemical shifts in para-disubstituted benzenes, and other experimental probes of charge distribution.

Introduction

In an earlier paper, we demonstrated that there is a systematic dependence of arene carbon chemical shifts on the electronic effects of carbenium-type substituents.[3] The systematic dependence is demonstrated for each position in an aryl group by determining the carbon chemical shift response, which is defined by plotting the ^{13}C chemical shifts in arylcarbenium ions vs. the ^{13}C chemical shifts at the para position in the analogous phenylcarbenium ions. For the hydrocarbon systems studied previously, the slope of the response was shown to be related to the charge distribution in the arylcarbenium

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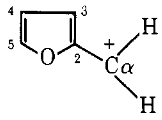
Table I. ^{13}C Chemical Shifts of 2-Furyl- and 2-Thienylcarbenium Ion Derivatives

substituent	C_2	C_3	C_4	C_5	C_α	CH_3
			A. 2-Furyl System			
$COCH_3$	150.3	114.2	110.2	143.3	181.8	25.4
CHO	150.4	118.3	110.5	145.0	173.8	
COCl	143.5	122.2	111.2	147.1	151.7	
$C(OH)CH_3^+$	147.3	145.2	120.3	164.3	190.9	21.1
$C(OH)CH_3^{+a}$	149.6	138.1	120.3	164.3	194.2	21.4
$CHOH^+$	147.6	152.4	121.7	168.4	173.7	
$CHOH^{+a}$	150.6	142.0	122.2	169.7	177.2	
$C(CH_3)_2^+$	159.8	152.1	126.9	179.0	193.1	25.8, 24.6
			B. 2-Thienyl System			
$COCH_3$	142.0	131.1	125.9	130.1	186.0	26.3
CHO	143.1	135.1	127.3	133.7	180.6	
$C(OH)CH_3^+$	132.7	149.3	131.5	155.1	198.7	22.5
$C(OH)CH_3^{+b}$	133.3	143.4	132.1	155.1	197.9	24.2
$CHOH^+$	134.8	158.1	135.0	163.0	186.5	
$C(CH_3)_2^+$	150.0	153.9	139.0	177.4	210.2	30.8, 28.2
$CHCH_3^+$	152.0	161.2	139.5	185.0	188.2	25.1
$CHCH_3^{+c}$		153.5	140.3	186.5	187.8	23.9

[a] Rotational isomer (~14%) with OH anti to furyl oxygen atom. [b] Rotational isomer (~10%) with OH anti to thienyl sulfur atom. [c] Rotational isomer (~10%) with CH_3 anti to thienyl sulfur atom.

ions. The arene positions which are predicted in simple resonance theory to become positively charged upon formation of the arylcarbenium ion exhibit steeper slopes than positions not conjugated with the carbenium center. Further, the ^{13}C chemical shift response slopes correlate with charge densities calculated by various MO methods.

In this paper we apply the same procedure to examine the ^{13}C chemical shift response in some heteroarenes. As with the hydrocarbon systems,[3] the observed patterns of response will be compared with MO calculations of electronic charge distribution. The four heteroarylcarbenium ion systems examined in this study, the 2-furyl- (**1**), 2-thienyl- (**2**), 2-benzofuryl (**3**), and 2-benzothienylcarbenium ion (**4**) systems, were chosen because of the availability of data regarding the effect of substituents on the solvolysis rates of 1-(heteroaryl)ethyl derivatives.[4-8] The substituent effects determined in the solvolytic rate studies are an independent, charge-related property which can be compared with the ^{13}C chemical shift responses measured from the stable ions.[9]



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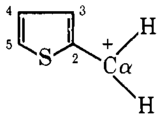

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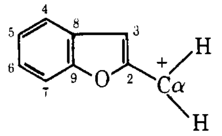

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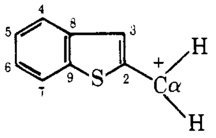

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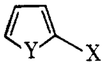
The results reported here are relevant to a problem raised by observations of nonadditivity of substituent chemical shifts in para-disubstituted benzenes.[10-14] In a series of para-disubstituted benzenes, XC_6H_4Y, the response of the ^{13}C chemical shifts at the carbon substituted by a group Y to changes in substituents X is dependent on the nature of Y. For instance, if Y is a group attached to the para carbon by a sulfur atom, the para carbon chemical shift is approximately twice as sensitive to the influence of X as when Y is a group attached by an oxygen atom.[12,13] The problem is whether the ^{13}C shifts reflect actual differences in electron densities, which would therefore be dependent on Y, or whether the nature of Y influences the sensitivity (in ppm/electron) of the chemical shift to changes in electron density.[10-14] The aryl systems examined in this paper are analogous to para-disubstituted benzenes, in that we can examine the ^{13}C chemical shift response of the carbons attached to Y to changes in carbenium-type substituents X. The advantage of such heterocycle systems is that the charge distribution at C_5 can be subjected to further experimental probing, by attaching additional substituents at C_5 (vide infra).



Carbon Chemical Shifts

Para-carbon chemical shifts, δ_C C_4-Ph, in the phenyl series of arylcarbenium ions serve as the reference points for establishing the carbon chemical shift response in other aryl systems. We have previously listed δ_C values for all positions in 25 species which could be considered as being derived from the phenylcarbenium ion by alteration of the side chain.[3] For our purposes, the category of carbenium-type substituent group consists of all substituents with a trigonal carbon bound to an aryl ring. The following is a list of para carbon shifts, δ_C C_4-Ph, for substituents which are used in the present study of heteroarylcarbenium ion systems, and also the ^{13}C chemical shift for benzene: H, 128.5; $COCH_3$, 132.7; CO_2H, 133.6; CHO, 134.0; COCl, 134.7; $C(OH)_2^+$, 141.5; $C(OH)CH_3^+$, 145.3; $CHOH^+$, 148.9; $C(CH_3)_3^+$, 155.9; $CHCH_3^+$, 161.6.

The carbon chemical shifts for 2-furyl- and 2-thienylcarbenium ion derivatives are given in Table I and the shifts for 2-benzofuryl- and 2-benzothienylcarbenium ion derivatives are presented in Table II. Assignments of carbon resonances were made from wide-band ^1H decoupled spectra, off-resonance or fully coupled spectra, and specific frequency ^1H decoupled spectra. The chief criteria for assignment were C–H coupling constants, long-range C–H coupling patterns, previously known chemical shifts, and consistency of shift positions within series of compounds. Full details of spectral analysis are given in the supplementary material accompanying this paper.[15]

Carbon Chemical Shift Responses

The carbon chemical shift response of the phenyl (Ph) system has been described previously,[3] but the results are summarized here in order to point out characteristic features of response in aryl systems. Figure 1 shows the carbon chemical shifts for each position in the phenyl ring plotted vs. the

Table II. ^{13}C Chemical Shifts of 2-Benzofuryl- and 2-Benzothienylcarbenium Ion Derivatives

carbon	substituent $COCH_3$	$C(OH)_2^+$	$C(OH)CH_3^+$	$C(CH_3)_2^+$	$CHCH_3^+$
			A. 2-Benzofuryl System		
C_2	153.3	136.7	146.4	158.1	160.0
C_3	113.7	130.1	141.7	149.3	158.1
C_4	124.1	125.8	127.3	129.7	131.0
C_5	124.6	126.6	127.3	129.1	129.9
C_6	128.9	134.7	139.8	148.3	152.3
C_7	113.0	113.2	113.7	114.9	115.3
C_8	127.8	126.6	128.2	132.0	133.2
C_9	156.2	159.4	162.6	170.3	173.2
C_α	188.8	171.2	194.8	197.6	171.7
CH_3	27.2		21.3	26.6, 25.7	19.7
			B. 2-Benzothienyl System		
C_2	144.7	121.1	133.4	147.3	150.1
C_3	130.6	142.8	152.6	156.4	165.8
C_4	126.7	128.2	130.1	134.1	135.4
C_5	125.8	127.0	127.5	129.7	130.3
C_6	128.2	132.5	136.0	142.2	145.3
C_7	123.7	122.8	123.5	124.8	125.7
C_8	139.9	137.9	139.1	142.2	142.3
C_9	143.3	147.5	152.6	163.7	167.4
C_α	192.8	175.8	204.5	214.6	191.4
CH_3	27.7		23.5	31.4, 28.7	25.6

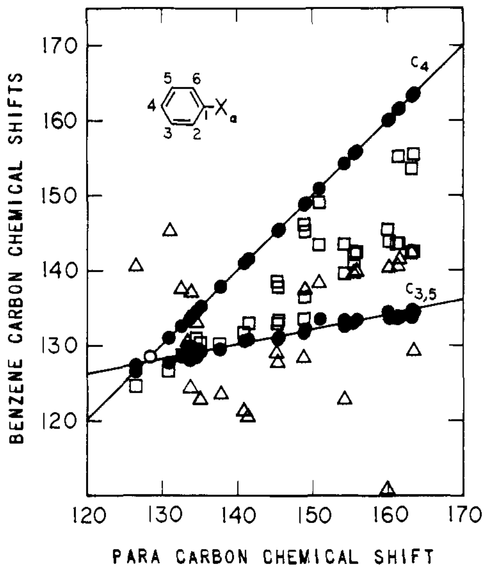


Figure 1. Carbon chemical shift response for the phenyl system. Chemical shift responses are determined by plotting the ^{13}C chemical shift for each ring position in an arylcarbenium ion vs. the ^{13}C shift at the para position in the analogous phenylcarbenium ion. The slope of a correlation line for a particular position measures the response of that position, relative to the para position, to changes in the side-chain structure. Open squares represent shifts of ortho carbons ($C_{2,6}$) and triangles represent the ipso carbons (C_1).

chemical shifts at the para position (δ_C C_4-Ph). The para-carbon shifts are plotted against themselves and therefore give a perfect correlation line with unit slope. This line of unit slope serves as the reference to which all other chemical shift responses can be compared. The response slope at a position C_x is defined by b in the equation

$$\delta_C\, C_x = b(\delta_C\, C_4\text{-Ph}) + i \qquad (1)$$

Plotting meta-carbon shifts, δ_C $C_{3,5}$-Ph, vs. δ_C C_4-Ph gives a correlation line of lesser slope ($m = 0.197$; see Table III). The plots of ortho ($C_{2,6}$) and ipso (C_1) carbon shifts vs. δ_C C_4-Ph show a great deal of scatter, although there is a clear tendency toward a positive slope in the δ_C $C_{2,6}$-Ph plot.

The scattered points in the plots of δ_C $C_{2,6}$-Ph and δ_C C_1-Ph vs. the reference δ_C C_4-Ph are representative of the general case: linear chemical shift responses are found only for aryl carbons in positions more remote from the site of substitution than the directly substituted ipso position and immediately adjacent, ortho-type positions. Typically, a remote position gives a linear chemical shift response with standard deviation of ca. 1 ppm or less in the linear relationship. Also typical is the greater response slope for a position (C_4-Ph) conjugated with the carbenium center, relative to a nonconjugated position ($C_{3,5}$-Ph).

The 2-Furyl System. The ^{13}C chemical shift responses for the 2-furyl (2-F) system are shown in Figure 2, in which the furan chemical shifts, δ_C C_n-2-F, from Table I are plotted vs. the reference para carbon shifts, δ_C C_4-Ph, from analogously substituted benzenes. The least-squares analysis of the responses is in Table III.

The 2-furyl system is similar to the phenyl system in that only two positions give good linear response patterns. The C_5-2-F line is steeper than the C_4-2-F line, which is typical for a conjugated position relative to a nonconjugated position. However, the slope of the C_4-2-F line is nearly as great as the C_4-Ph slope, and is considerably larger than the slope for the analogous $C_{3,5}$-Ph position. The ortho-type position, C_3-2-F, gives a steep response, but with the substantial scatter characteristic of positions sterically proximate to the substituents. The δ_C for the ipso position, C_2-2-F, also give a scattered pattern when plotted vs. δ_C C_4-Ph. Contrary to the results for the other heteroaryl systems examined here, and for the 1- and 2-naphthyl systems,[3] the δ_C C_2-2-F do not correlate well with the analogous ipso-position shifts, δ_C C_1-Ph, from the phenyl series ($m = 0.56$, cc $= 0.585$).

The 2-Thienyl System. Carbon chemical shift responses for the 2-thienyl (2-T) system are shown in Figure 3 and the results are listed in Table III. The two positions remote from the site of substitution, C_5-2-T and C_4-2-T, give linear responses, with the slope for C_5 being steeper than for C_4, as expected. The usual scatter is seen in the response for the ortho-type position, C_3-2-T, although a distinct trend toward a positive slope is evident. The δ_C C_2-2-T give the expected scatter in the response, but a fair correlation is obtained in a linear relationship with δ_C C_1-Ph ($m = 1.35$, cc $= 0.970$).

Table III. Least-Squares Analysis of Chemical Shift Response Patterns in Heteroarylcarbenium Ions (eq 1)

position	response slope	intercept	SD[a]	cc[b]	n[c]
		A. Phenyl System[d]			
1	0.124	113.6	8.47	0.174	25
2,6	0.669	39.7	4.10	0.879	36
3,5	0.197	102.4	0.52	0.977	28
4	1.000	0.0	0.00	1.000	25
		B. 2-Furyl System			
2	0.311	105.4	4.15	0.565	8
3	1.722	−111.1	4.85	0.956	8
4	0.750	10.6	0.61	0.996	8
5	1.564	−63.9	0.84	0.998	8
		C. 2-Thienyl System			
2	0.321	94.2	7.81	0.430	7
3	0.864	20.3	5.19	0.896	8
4	0.491	61.1	0.88	0.989	8
5	1.926	−124.6	1.09	0.995	8
		D. 2-Benzofuryl System			
2	0.469	81.7	9.05	0.567	5
3	1.469	−78.0	4.25	0.977	5
4	0.243	91.7	0.25	0.997	5
5	0.181	100.7	0.22	0.996	5
6	0.832	18.2	0.89	0.997	5
7	0.087	101.2	0.26	0.976	5
8	0.224	96.5	1.45	0.899	5
9	0.622	72.7	1.04	0.992	5
		E. 2-Benzothienyl System			
2	0.495	66.4	12.20	0.474	5
3	1.136	−17.7	3.76	0.970	5
4	0.322	83.4	0.62	0.990	5
5	0.163	104.0	0.22	0.995	5
6	0.605	47.7	0.55	0.998	5
7	0.082	112.0	0.75	0.824	5
8	0.032	136.2	2.65	0.160	5
9	0.891	23.6	1.69	0.990	5

[a] Standard deviation. [b] Correlation coefficient. [c] Number of chemical shifts included in the analysis. [d] Data from ref 3.

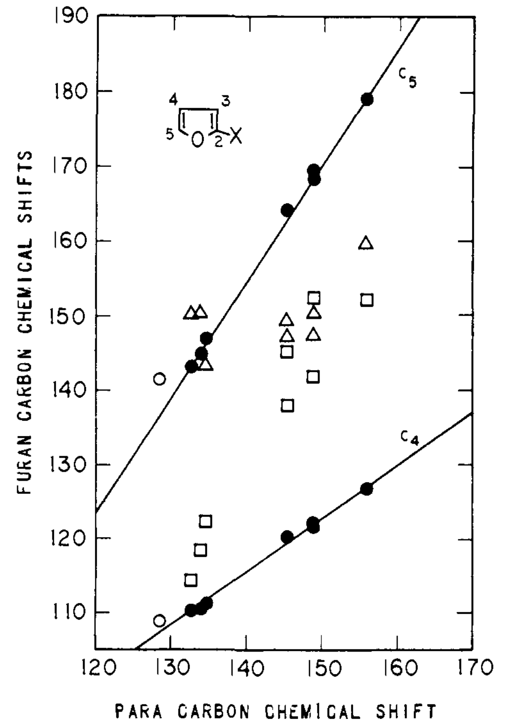
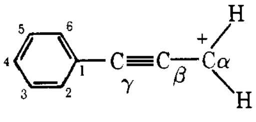


Figure 2. Carbon chemical shift responses for the 2-furyl system: △, C_2; □, C_3.

The 2-Benzofuryl System. Figure 4 shows the plot of ^{13}C chemical shifts in the 2-benzofuryl series vs. the reference chemical shifts for the para position in the phenyl series. The least-squares analysis is presented in Table III.

The 2-benzofuryl (2-BF) ring has six positions which are remote from the site of substitution. Five of these positions (C_4, C_5, C_6, C_7, and C_9) give linear chemical shift responses. C_8-2-BF gives a curved response which is similar to the curved patterns observed for the analogous C_1-PhE position in the phenylethynyl series (**5**) and C_{8a}-2-N in the 2-naphthyl series (**6**).[3]



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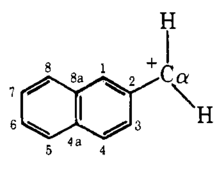

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For the 2-BF positions which give linear responses, the slopes for the positions (C_4, C_6, and C_9) conjugated with the carbenium center are steeper than for the nonconjugated positions (C_5 and C_7). C_3-2-BF is also a conjugated position which exhibits a steep response, but it shows the scatter typical of an ortho-type position. The ipso position also gives the usual scattered pattern, but the δ_C C_2-2-BF do correlate well with the analogous δ_C C_1-Ph ($m = 1.07$, cc = 0.994).

The 2-Benzothienyl System. The carbon chemical shift patterns for the 2-benzothienyl system (2-BT), illustrated in

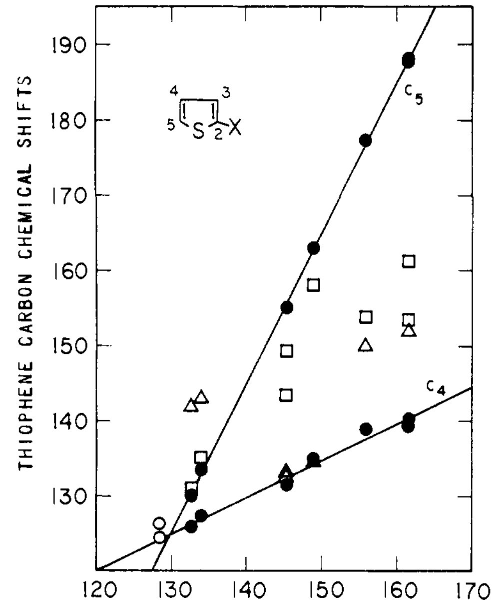


Figure 3. Carbon chemical shift responses for the 2-thienyl system: △, C_2; □, C_3.

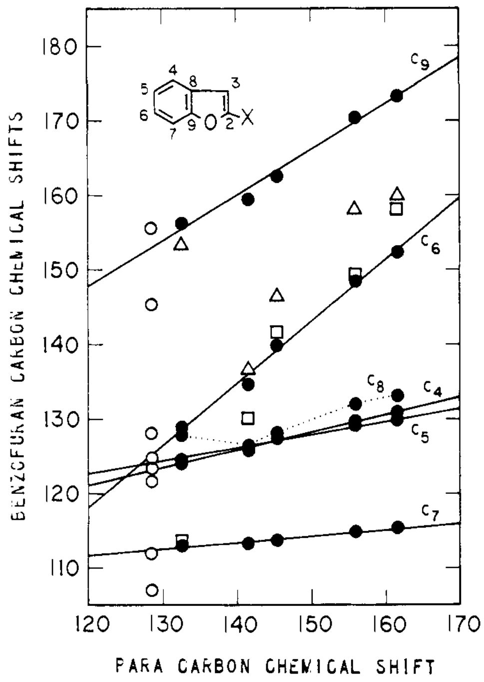


Figure 4. Carbon chemical shift responses for the 2-benzofuryl system: △, C_2; □, C_3.

Figure 5 and described in Table III, are very similar to the pattern in the 2-benzofuryl series. Five positions give linear responses. The positions (C_4, C_6, and C_9) conjugated with the carbenium center have steeper response slopes than the nonconjugated positions (C_5 and C_7). C_8-2-BT has the same type of curved pattern as C_8-2-BF. C_3-2-BT displays a trend toward a positive slope, but also has considerable scatter in its response. C_2-2-BT gives the scattered pattern typical of an ipso position, while giving an excellent correlation with the δ_C C_1-Ph (m = 1.35, cc = 0.999).

Discussion

In several respects, the behavior of the heteroaryl systems parallels that of the hydrocarbon aryl systems previously examined.[3] Linear carbon chemical shift responses are found at most positions in the heteroarylcarbenium species when those positions are not the directly substituted ipso position or the adjacent ortho-type positions (Figures 1-5). In other words, the carbons in these ring systems are deshielded by electron-withdrawing, carbenium-type substituents in proportion to the effect that such substituents have on the para position in benzene, which serves as the reference. Qualitatively, the response slopes (Table III) reflect the expectation that positions conjugated with the carbenium center should have steeper chemical shift response slopes than nonconjugated positions, owing to the greater development of positive charge. For instance, based on resonance structures shown below for the 2-furylcarbenium ion, greater charge development is expected at the 5 position than at the 4 position, and the response slopes are in agreement (m = 1.564 for C_5-2-F and m = 0.750 for C_4-2-F).

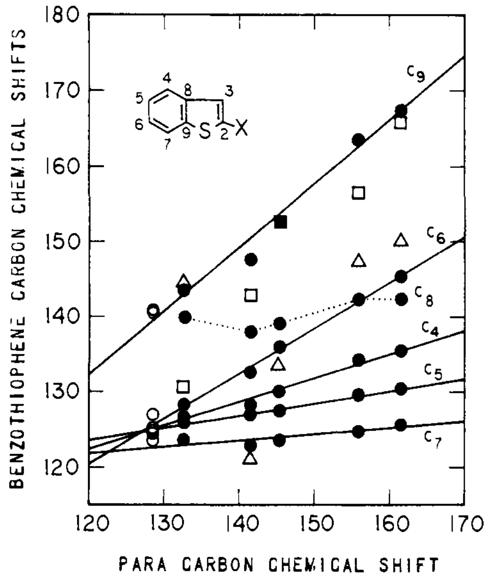
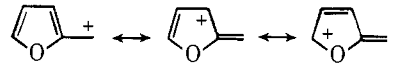


Figure 5. Carbon chemical shift responses for the 2-benzothienyl system: △, C_2; □, C_3.



The results presented here and in the previous study[3] clearly demonstrate a systematic dependence of carbon chemical shifts on the electron-withdrawing capability of carbenium-type substituents in several aryl systems. Since this conclusion is derived through comparison with chemical shifts at the para position in benzene, and since it is well recognized that para-carbon shifts are linearly related to charge densities at the para carbon,[16-21] it is tempting to conclude that the slope of the chemical shift response could serve as an empirical measure of charge density in the arylcarbenium ions. In the phenyl-, phenylethynyl-, 1-naphthyl-, and 2-naphthylcarbenium ions, a good correlation was found between the response slopes and calculated charge densities.[3]

However, the linear response patterns observed here do not guarantee that each position will have the same proportionality constant for the dependence of ^{13}C shifts on charge. In fact, close examination of the slopes in Table III reveals a few disturbing results. For example, the response slope for C_5 in thiophene suggests that C_5 in the 2-thienylcarbenium ion has nearly twice as much positive charge as the analogous C_4 in the phenylcarbenium ion. Earlier, Gronowitz et al. noted a nearly double sensitivity to substituent effects at C_5 in thiophene relative to C_4 in benzene.[22] Also, C_4 in the 2-furylcarbenium ion is predicted to develop considerable positive charge even though it is not a conjugated position. These results cer-

Table IV. Calculated Changes in Charge Density for Ar → $ArCH_2^+$

position	SCF-π	CNDO/2 total	CNDO/2 π	CNDO/2 regional
		A. Phenyl System		
C_α	0.436	0.231	0.502	0.405
C_1	−0.013	−0.004	−0.050	0.001
$C_{2,6}$	0.147	0.109	0.178	0.158
$C_{3,5}$	0.042	−0.022	−0.025	0.039
C_4	0.200	0.140	0.242	0.199
		B. 2-Furyl System		
O_1	−0.008	0.033	−0.007	0.033
C_2	0.030	0.034	−0.010	0.026
C_3	0.279	0.207	0.377	0.279
C_4	0.061	−0.023	−0.030	0.053
C_5	0.264	0.176	0.306	0.261
C_α	0.374	0.143	0.364	0.348
		C. 2-Thienyl System		
S_1	0.039	0.142	0.028	0.142
C_2	0.016	−0.009	−0.032	0.016
C_3	0.292	0.204	0.361	0.267
C_4	0.040	−0.029	−0.041	0.044
C_5	0.232	0.136	0.288	0.209
C_α	0.380	0.176	0.395	0.355
		D. 2-Benzofuryl System		
O_1	−0.017	0.022	−0.023	0.022
C_2	0.017	0.005	−0.038	0.002
C_3	0.299	0.225	0.414	0.280
C_4	0.072	0.073	0.104	0.113
C_5	0.045	−0.003	0.002	0.045
C_6	0.118	0.087	0.150	0.133
C_7	0.023	−0.012	−0.026	0.033
C_8	−0.001	−0.034	−0.068	−0.034
C_9	0.090	0.085	0.130	0.085
C_α	0.350	0.134	0.356	0.321
		E. 2-Benzothienyl System		
S_1	0.010	0.102	−0.008	0.102
C_2	0.010	−0.035	−0.044	−0.038
C_3	0.298	0.221	0.396	0.267
C_4	0.075	0.069	0.100	0.105
C_5	0.042	−0.005	−0.002	0.040
C_6	0.117	0.080	0.137	0.124
C_7	0.026	−0.009	−0.022	0.032
C_8	−0.017	−0.038	−0.074	−0.038
C_9	0.077	0.063	0.109	0.063
C_α	0.362	0.180	0.407	0.344

tainly need verification through comparison with calculated charges or, preferably, some independent measure of charge distribution.

In Table IV are listed changes in charge densities (Δq_i) calculated for the formation of arylcarbenium ions from the neutral arenes. The changes in charge densities are the quantities of interest because the experimental quantities are the changes in δ_C induced by progressively stronger electron-withdrawing substituents, leading toward the parent arylcarbenium ions. Calculations were performed with a PPP SCF-π method[23] and the CNDO/2 method,[24] using the same ring geometries[25] for the cations as for the arenes. The CNDO/2 results have been analyzed for π charge densities, total carbon charge densities ($\pi + \sigma$), and regional charge densities, which are defined as the sum of the charges on a carbon atom and any hydrogen atoms attached to it.[26] An excellent correlation may be seen in Table IV between CNDO/2 regional charges and PPP SCF-π charges.

The best correlation of chemical shift response slopes in the hydrocarbon systems was with the SCF-π charges.[3] The same is true for the heteroaryl systems examined here. Figure 6 shows a plot of response slopes (for the positions that give low SDs in Table III) against Δq_i from the SCF-π method. The line in Figure 6 is the previously determined correlation line for the hydrocarbon series.[3] Clearly, there is considerable scatter in the plot, although a rough correlation is evident. Even considering the low level of the calculations (in which no geometry optimization is performed, the choice of parametrization can be questioned, the adequacy of the treatment of electron repulsions involving heteroatom lone pairs is doubtful, etc.), some of the points deviate from the line to such an extent that it seems unlikely that the source of the deviations is inaccurate MO calculations of the π charges.

The most deviant point (labeled C_5-2-T) in Figure 6 is for the 5 position in the 2-thienyl ring, where the response slope is much too large for the calculated Δq_i. The next most deviant point (C_9-2-BT) is for the C_9 position in the 2-benzothienyl ring, which is also adjacent to the sulfur atom of a thiophene ring. *If the ^{13}C chemical shifts at these positions adjacent to sulfur atoms are linearly related to π charge densities, then the proportionality constant in the relationship with charge must be considerably greater for these positions than for positions in hydrocarbon aryl systems.* It is noteworthy that the response slopes for the benzo portion (C_4, C_5, C_6, and C_7-2-BT) of the benzothienyl system fall very close to the hydrocarbon correlation line.

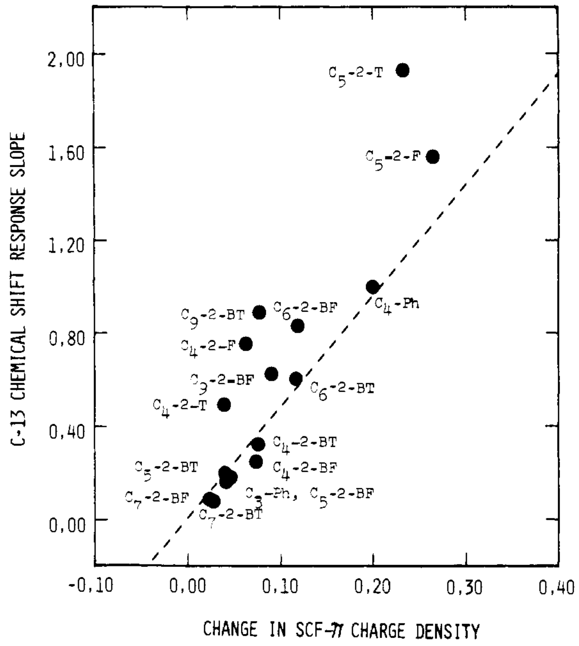


Figure 6. Plot of carbon chemical shift response slopes vs. calculated changes in SCF-π charge density. The response slopes are the slopes of the lines in Figures 1-5. Changes in charge for each position are calculated for the formation of an arylcarbenium ion from the neutral arene. The dotted line is the correlation line from the hydrocarbon systems studied previously[3] and is not the correlation line for the data shown.

Another observation which suggests a difference in the susceptibility of sulfur-adjacent positions to substituent influence is the larger slope for the plots of ipso carbon shifts in the 2-thienyl and 2-benzothienyl derivatives vs. the analogous phenyl ipso carbon shifts, when compared with the plots of 1-naphthyl (1-N), 2-naphthyl (2-N), and 2-benzofuryl ipso shifts vs. phenyl ipso shifts. The slopes of δ_C C_2–2-T and δ_C C_2–2-BT vs. δ_C C_1–Ph are both 1.35, while the slopes of δ_C C_1–1-N, δ_C C_2–2-N, and δ_C C_2–2-BF vs. δ_C C_1–Ph are closer to one (1.05, 1.11, and 1.07, respectively). Gronowitz et al.[22] noted the same high sensitivity for C_2 in neutral, 2-substituted thiophenes.

Another approach to evaluate the meaning of the response slopes, which avoids the problem of the adequacy of the molecular orbital calculations, is to compare them with other empirical properties which are charge dependent. For instance, values of ^{19}F chemical shifts in para-substituted fluorobenzenes correlate well with fluorine π-electron charges[21] and also with the para-carbon shifts for the corresponding substituted benzenes.[21,27] Interestingly, a study of 2-fluorothiophenes with conventional substituents in the 5 position showed that the ^{19}F chemical shifts were only slightly more sensitive than in para-substituted fluorobenzenes,[28,29] in contrast to the nearly double sensitivity of the carbon chemical shifts discussed above. Another such comparison can be based on substituent effects in the solvolysis reactions of 1-arylethyl derivatives. The effect of substituents at C_5 in thiophene on the rate of solvolysis of 1-(2-thienyl)ethyl p-nitrobenzoates ($\log k_{CH_3}/k_H = 1.91$) is only slightly larger than the effect of para substituents on the solvolysis of 1-phenylethyl chlorides ($\log k_{CH_3}/k_H = 1.76$).[8] Thus, examination of other charge-dependent phenomena does not indicate unusually high charge development at C_5 in 2-thienyl systems. These empirical comparisons therefore are consistent with the suggestion that the C_5 chemical shift in 2-thienyl derivatives is more sensitive to substituent effects than can be explained by charge effects alone.

Fringuelli et al.[30] pointed out systematic regularities in the dependence of ^{13}C shifts on substituents in five-membered heteroaromatics, comparable to our linear patterns of response. They found that the ease of transmission of substituent effects to the 5 carbon increased with the increase in atomic weight of the heteroatom, i.e., furan < thiophene < selenophene < tellurophene. In studies of para-disubstituted benzenes, Lynch noted an analogous dependence of the chemical shift sensitivity on the nature of the attached atom.[13] When substituents X are varied in XC_6H_4Y, the response of the para-carbon chemical shift is dependent on the Y group attached at the para carbon. Increasing sensitivities were observed for the following sequences of the attached atom in Y groups: O < S < Se; F < H < Cl < Br < I; C < Si < Ge < Sn. Lynch concluded tentatively that the different sensitivities were not due to differing ranges of ground-state variations in electron density at the para carbon. Rather, the ionization potential of Y was postulated to have a local effect, at the para carbon, on the excitation energy term ΔE of the paramagnetic shielding expression[31] for ^{13}C shifts. This would have the effect of altering the ppm/electron sensitivity to charge density differences.

The postulated influence of Y on excitation energies, whether as a benzene substituent or in a heteroarene, must be restricted to the attached carbons. Using the Karplus-Pople[31] expression for the paramagnetic contribution to the shift, which includes an inverse dependence on ΔE (the excitation energy of the shielding electrons), researchers have sought to improve correlations between calculated and observed shifts by adjusting a value of ΔE, which is used as an average value for a molecule.[32-34] However, Farnum has pointed out that the ΔE correction results in about the same change in shift at each position in a five-membered heterocycle.[35] An adjustment in an average ΔE cannot account for the greater sensitivity to substituent effects at C_5 in thiophene relative to furan because the reverse is the case at C_4 in these heterocycles. Also, the benzo ring carbons in both benzothiophene and benzofuran follow reasonably well the charge correlation line established in the pure hydrocarbon systems. Thus, any theoretical treatment of the unusual sensitivity of the carbons adjacent to sulfur must explain it as a local effect.

Experimental Section

Sample Preparation and ^{13}C NMR Spectra. The ^{13}C NMR spectra were obtained on Varian Associates Model XL-100 and HA-100 spectrometers operated in the pulsed Fourier transform mode. Details of the instrumentation and methods have been described elsewhere.[36,37] External (capillary) $Si(CH_3)_4$ was used as the chemical shift reference. The spectra of the carbocations were measured at −60 or −80 °C. Spectra of the neutral species were measured at the ambient operating temperature.

In the 2-furyl series, high-purity commercial samples of 2-acetylfuran, 2-furancarboxylic acid chloride, and furfural were used as ~25% solutions in CCl_4. 2-F-$CHOH^+$ (~10% solution) was prepared by the dropwise addition of furfural in SO_2ClF at −78 °C (dry ice-acetone bath temperature) to a 1:1 v/v solution of FSO_3H in SO_2ClF at −78 °C. The ~10% solution of 2-F-$C(CH_3)_2^+$ was obtained by the similar addition of 2-(2-furyl)-2-propanol in SO_2ClF to FSO_3H-SO_2ClF. The alcohol precursor was synthesized by the reaction of 2-acetylfuran with methylmagnesium iodide.

In the 2-thienyl series, 2-acetylthiophene and 2-thiophenecarboxaldehyde were high-purity samples used at ~25% solutions in CCl_4. The ions were all obtained by the addition of a solution of the precursor in SO_2ClF at −78 °C to a 1:1 v/v solution of FSO_3H in SO_2ClF at −78 °C (ion, precursor): 2-T-$C(OH)CH_3^+$, 2-acetylthiophene; 2-T-$CHOH^+$, 2-thiophenecarboxaldehyde; 2-T-$C(CH_3)_2^+$, 2-(2-thienyl)-2-propanol; 2-T-$CHCH_3^+$, 1-(2-thienyl)ethanol. 2-(2-Thienyl)-2-propanol was synthesized from thiophene by lithiation in ether with n-butyllithium (1.6 N in hexane, Aldrich) followed by reaction with anhydrous acetone. 1-(2-Thienyl)ethanol was obtained by $NaBH_4$ reduction of 2-acetylthiophene.

In the 2-benzofuryl series, 2-acetylbenzofuran was a high-purity commercial sample used as an ~25% solution in $CDCl_3$. As described for the 2-furyl and 2-thienyl series, the ions were all prepared as solutions in FSO_3H-SO_2ClF (ion, precursor): 2-BF-$C(OH)_2^+$, 2-benzofurancarboxylic acid; 2-BF-$C(OH)CH_3^+$, 2-acetylbenzofuran;

2-BF-C(CH$_3$)$_2^+$, 2-(2-benzofuryl)-2-propanol; 2-BF-CHCH$_3^+$, 1-(2-benzofuryl)ethanol. The alcohol precursors were synthesized from 2-acetylbenzofuran by reaction with methylmagnesium iodide to give 2-(2-benzofuryl)-2-propanol, and by reduction with NaBH$_4$ to give 1-(2-benzofuryl)ethanol.

In the 2-benzothienyl series, all precursors were synthesized from 2-lithiobenzothiophene obtained in a lithiation of benzothiophene in ether using *n*-butyllithium in hexane.[38] The subsequent reaction with acetaldehyde yielded 1-(2-benzothienyl)ethanol, and this alcohol was oxidized to 2-acetylbenzothiophene with MnO$_2$-C.[39] Carbonation of 2-lithiobenzothiophene with dry ice and workup with 6 N HCl gave 2-benzothiophenecarboxylic acid. Reaction of 2-lithiobenzothiophene with acetone gave 2-(2-benzothienyl)-2-propanol. The spectrum of 2-acetylbenzothiophene was obtained from an ~25% solution in CDCl$_3$, and the spectra of the ions were obtained from FSO$_3$H-SO$_2$ClF solutions prepared as described above for the other heteroaryl systems.

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Supplementary Material Available: Detailed discussion of ^{13}C peak assignments in the heteroarylcarbenium ions (7 pages). Ordering information is given on any current masthead page.

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