

Patterns of Carbon-13 Chemical Shift Response to Substituent Effects in Arylcarbenium Ions. The Phenyl, Phenylethynyl, and Naphthyl Systems¹

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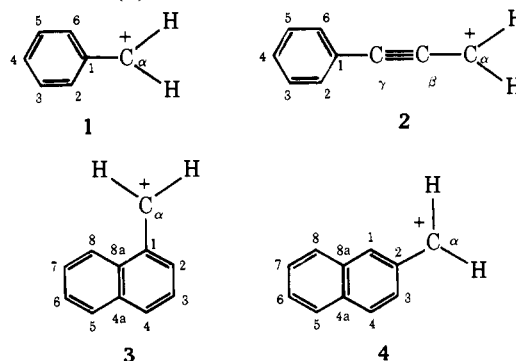
Abstract: An empirical treatment of ¹³C chemical shifts in arylcarbenium ions is presented which demonstrates that there is a systematic dependence of arene carbon chemical shifts on the electronic effects of carbenium-type substituents. The relationship is evident not only at positions formally conjugated with the carbenium center, such as the para position in benzene, but at most positions remote from the site of substitution in several arylcarbenium ion systems. The systematic dependence is demonstrated for each position in an aryl group by determining the carbon chemical shift response pattern, which is defined as the rate of change in ¹³C chemical shift relative to the rate of change at the para position of benzene. The response patterns are established by plotting chemical shifts for a series of arylcarbenium ions vs. the chemical shifts at the para position of the analogously substituted benzenes. Comparison of the chemical shift response patterns with MO calculations of the changes in charge distribution upon formation of an arylcarbenium ion from a neutral precursor shows a linear relationship between the slopes of the response patterns and the changes in charge density.

The best quantitative correlations between carbon chemical shifts and calculated charge densities have been observed for carbon atoms in monocyclic aromatic ring systems^{3,4} and the para carbons of monosubstituted benzenes.⁵⁻⁹ Nelson, Levy, and Cargioli reported an excellent correlation covering a range of 16.5 ppm between the para carbon chemical shift and CNDO/2 calculated charge densities for the para carbon.⁸ We have recently extended this correlation to cover a total range of 45 ppm by measuring the chemical shifts for a series of monosubstituted benzenes in which the substituent bears a formal positive charge.⁹ However, attempts to correlate other carbon chemical shifts with molecular orbital calculations of π or total electron densities have met with only limited success even when other important influences¹⁰ such as hybridization, neighboring group effects, and steric interactions are held constant by confining the comparison of chemical shifts to closely related series of compounds. Part of the failure to observe precise correlations with calculated charges may be due to the inaccuracy of calculated wave functions or problems of population analysis.^{11,12} The procedure in most studies involves comparing chemical shifts for a series of compounds with charge densities or theoretical shieldings¹³⁻¹⁵ calculated for each individual compound in the series. Thus, the MO calculations are expected to accurately describe molecules containing a variety of substituents or structural types. The success of these comparisons with theoretical quantities is highly dependent on the MO method used.¹⁵⁻²²

In this paper we describe a procedure applicable to arylcarbenium ions, which first establishes the existence of a systematic dependence of carbon shifts on electronic effects of carbenium-type substituents, before any comparison with MO calculations is made. The chemical shifts (δ_C) of the carbon atoms in a particular arene system are measured for a series of arylcarbenium ions in which the demand for electron donation from the arene to the carbenium center is progressively increased by altering the substituents at the carbenium center. The sensitivity of the δ_C at each position in the arene to the substituent changes is established by comparing the changes in arene δ_C to the changes in δ_C at the para position of the analogously substituted benzenes. Thus, the δ_C at the para position of phenyl derivatives, which are known to correlate well with charge densities, are used as a measure of the electron-withdrawing capability of

substituents. For each position in an aryl group, this procedure determines the chemical shift response pattern, defined as the rate of change in chemical shifts relative to the rate of change at the para position of benzene.

The carbon chemical shift response patterns thus established can be compared with calculated changes in charge distribution upon formation of an arylcarbenium ion from a neutral precursor. The *changes* in charge distribution are the quantities of interest simply because the experimental quantities are the *changes* in δ_C induced by progressively stronger electron-withdrawing substituents, leading toward the parent arylcarbenium ion. Although all attempts to prepare the stable, parent phenylcarbenium ion (benzyl cation) and other primary, unsubstituted arylcarbenium ions have not succeeded, it is expected that chemical shift data for such ions would merely extend the patterns already established and thus are not essential to the analysis. Four arylcarbenium ion systems are considered in this paper: phenyl- (1), phenylethynyl- (2), 1-naphthyl- (3), and 2-naphthylcarbenium ions (4).



Carbon Chemical Shifts

The Phenyl System. Although carbon chemical shifts have been measured for a large number of monosubstituted benzenes, only species which can be treated as being derived from the phenylcarbenium ion by alteration of the side chain will be considered here. For our purposes, the category of carbenium-type substituent groups consists of all substituents with a trigonal (sp^2 hybridized) carbon bound to the phenyl ring, including neutral substituents such as the acetyl and carboxaldehyde groups, and cationic substituents such as the dimethylcarbenium and methylcarbenium

Table I. ^{13}C Chemical Shifts of Phenylcarbenium Ion Derivatives^a

Substituent	C ₁	C _{2,6}	C _{3,5}	C ₄
H ^b	128.5	128.5	128.5	128.5
C(CH ₃)CH ₂ ^c	140.5	124.6	127.2	126.5
CONH ₂ ^c	132.5	126.5	127.7	131.0
COCH ₃	137.6	128.6	128.5	132.7
COOH	130.6	130.0	128.5	133.6
COF ^c	124.2	130.1	127.8	133.8
CHO	137.1	129.8	129.1	134.0
COCl	133.1	130.9	128.5	134.7
COCF ₃	122.9	130.3	129.2	135.2
C(OH)NH ₂ ^{+c}	123.4	130.1 ^d	129.2 ^d	137.8
C(OH)OCH ₃ ⁺	121.3	131.8	130.6	140.9
C(OH) ₂ ⁺	120.4	133.0	130.8	141.5
C(OH)CH ₃ ⁺	129.0	138.5, 133.0	130.9	145.3
C(OH)CH ₂ CH ₃ ⁺	127.9	137.8, 133.3	131.1	145.4
CHOH ⁺	128.4	146.1, 133.7	131.8	148.9
CH(c-C ₃ H ₅) ⁺	137.6	145.2, 136.4	132.2	149.0
CHC ₆ H ₅ ⁺	138.3	149.1, 143.4	133.7	150.9
C(OH)CF ₃ ⁺	122.9	143.5, 139.6	133.3, 132.6	154.2
C(CH ₃)CH ₂ CH ₃ ^{+c}	139.5	142.0, 140.9	132.8	155.5
C(CH ₃) ₂ ⁺	140.0	142.4	133.3	155.9
CF ₂ ⁺	110.9	145.5	134.5	160.0
CCl ₂ ⁺	140.4	143.9	133.7	160.1
CHCH ₂ CH ₃ ^{+c}	140.4	155.0, 143.6	133.8, 133.6	161.3
CHCH ₃ ⁺	141.5	155.1, 143.6	133.8	161.6
CHCl ⁺	142.3	153.5, 142.3	124.8, 133.8	163.2
CHF ⁺	129.3	155.3, 142.4	134.6	163.5

^a δ_{C} , ppm from tetramethylsilane. Data for uncharged benzenes from ref 8, and data for carbenium ions from ref 9, unless otherwise noted. ^b Shift for benzene was not used in correlation in Table IV. ^c Shifts determined in this study. ^d Interchangeable values.

groups. The limitation to this type of substituent is intended to minimize variations in the inductive effect or other possible substituent influences on chemical shifts. The δ_{C} for phenylcarbenium ion (Ph) derivatives are listed in Table I. The para carbon shifts, $\delta_{\text{C}} \text{C}_4\text{-Ph}$, will serve as the numerical reference points for the electron-withdrawing effects of the substituents, whether attached to the phenyl ring or other aryl systems.

The Phenylethynyl System. Carbon chemical shifts measured for phenylethynylcarbenium ion (PhE) derivatives are listed in Table II. The assignment of resonances was straightforward, with assignments made by using off-resonance decoupling, relative peak intensities, peak positions in analogy with similar compounds, and long-range spin-spin coupling constants, as noted in the table.

The 1- and 2-Naphthyl Systems. The δ_{C} measured for 1-

naphthylcarbenium ion (1-N) and 2-naphthylcarbenium ion (2-N) derivatives are listed in Table III. The considerations which led to the assignment of resonances in these series are discussed in detail in the supplementary material²³ accompanying this paper, because of the complexity of the spectra of naphthalene derivatives and because of a disagreement with the assignment of resonances for 1-acetylnaphthalene and 2-acetylnaphthalene, as made by Wells, Arnold, and Doddrell.²⁴ The assignments by Wells et al. for the acetyl compounds were made by comparing the observed changes in chemical shifts induced by methyl substitution with the changes expected on the basis of additivity of substituent effects on chemical shifts. Our reassignments were made primarily on the basis of characteristic long-range C-H coupling patterns^{25,26} observed in the fully C-H coupled spectra. Our assignments do not adversely affect their observations of substituent additivity effects in naphthalenes, if the resonances in the methyl derivatives are also reassigned.²³

Carbon Chemical Shift Response Patterns

The Phenyl System. The carbon chemical shift response patterns for the various positions in an aryl system are established by plotting all of the ring δ_{C} values for each arylcarbenium ion derivative vs. the $\delta_{\text{C}} \text{C}_4\text{-Ph}$ of the analogously substituted benzene. Figure 1 shows the graph of all phenyl δ_{C} vs. $\delta_{\text{C}} \text{C}_4\text{-Ph}$. 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 response patterns can be compared. Plotting meta carbon shifts, $\delta_{\text{C}} \text{C}_{3,5}\text{-Ph}$, vs. $\delta_{\text{C}} \text{C}_4\text{-Ph}$ gives a correlation line of lesser slope ($m = 0.197$; see Table IV). The lesser slope indicates that the meta position is less sensitive to the electronic effects of substituents than the para position, in qualitative agreement with the expectation from simple resonance theory of charge delocalization to the para position and not to the meta position. The relation of chemical shift response patterns to calculated charge distributions will be discussed in a later section, along with results from other systems.

The plots of ortho (C_{2,6}) and ipso (C₁) carbon shifts vs. $\delta_{\text{C}} \text{C}_4\text{-Ph}$ show a great deal of scatter, although there is a clear tendency toward a positive slope in the $\delta_{\text{C}} \text{C}_{2,6}\text{-Ph}$ plot, as indicated in Table IV and Figure 1. The scatter is apparently due to influences on chemical shifts other than π system electronic effects. For instance, several of the phenyl derivatives have nonequivalent ortho carbon resonances (Table I), indicative of an important shielding contribution

Table II. ^{13}C Chemical Shifts of Phenylethynylcarbenium Ion Derivatives

Substituent	C _{α}	C _{β}	C _{γ}	C ₁	C _{2,6}	C _{3,5}	C ₄	Additional
H ^a		81.2	84.9	121.7	132.1	128.9	129.5	
CONH ₂	156.0	82.0	88.0	119.5	133.3	129.5	131.6	
COCH ₃	186.8	88.0	91.8	119.4	133.5	129.3	131.7	CH ₃ , 32.0
COOH	154.6	81.3	85.4	119.6	133.4	129.4	131.5	
COOCH ₂ CH ₃ ^a	153.9	80.9	85.3	119.7	133.1	129.0	131.1	CH ₂ , 62.1; CH ₃ , 13.6
COF ^b	149.7	83.1	94.2	117.5	133.5	128.7	132.4	
CHO ^c	178.9	87.6	97.0	118.2	133.6	129.1	132.2	
C(OH)NH ₂ ⁺	159.1	75.0	106.4	116.4	134.5	129.8	134.5	
C(OH) ₂ ⁺	167.5	76.8	112.5	115.5	136.2	130.1	136.2	
C(OH)OCH ₂ -CH ₃ ^{+a}	165.8	79.5	109.5	115.6	135.6	129.7	136.2	CH ₂ , 75.9; CH ₃ , 12.8
C(OH)CH ₃ ⁺	202.9	91.5	134.0	116.0	137.8	130.3	138.4	CH ₃ , 29.9
CHOH ^{+d}	187.6	95.1	143.7	115.9	138.7	130.3	139.8	
C(CH ₃) ₂ ⁺	237.1	123.5	199.4	119.9	141.7	131.4	145.5	CH ₃ , 38.5

^a Chemical shift data not used for correlation in Table IV. Ethyl ester data not available in the phenyl series, but compared with methyl benzoate in Figure 2. ^b Coupling data (in Hz): ³J_{C γ -F} = 14.0; ²J_{C β -F} = 103.1; ¹J_{C α -F} = 313.9. ^c Coupling data (in Hz): ³J_{C γ -H} < 2; ²J_{C β -H} = 30.1; ¹J_{C α -H} = 196.6. ^d Coupling data (in Hz): ³J_{C γ -H} < 2; ²J_{C β -H} = 13.0; ¹J_{C α -H} = 208.1; C₁ was observed as a broadened triplet, J = 7.0, due to coupling to the meta protons.

Table III. ^{13}C Chemical Shifts of 1- and 2-Naphthylcarbenium Ion Derivatives

Carbon	Substituent							
	COCH_3	CHO	COCl	C(OH)_2^+	C(OH)CH_3^+	CHOH^+	$\text{C(CH}_3)_2^+$	CHCH_3^+
(a) 1-Naphthyl System ^a								
C_1	135.8	131.8	<i>b</i>	117.3	124.6	124.0	140.4	136.4 ^c
C_2	129.4	137.0	136.5	136.9	148.3	155.4	148.8	149.6
C_3	125.0	125.3	125.4	124.8	126.2	126.9	127.2	128.5
C_4	133.5	135.6	137.3	142.3	146.3	151.0	157.5	165.4
C_5	129.0	129.0	129.9	130.2	131.3	131.7	132.7	133.4
C_6	127.0	127.4	128.0	128.3	128.8	129.6	129.0	129.6
C_7	128.6	129.4	130.4	131.3	133.8	134.9	135.2	138.0
C_8	126.7	125.3	125.9	124.1	125.7	125.8	125.9	121.7
C_{4a}	134.6	134.1	134.6	133.8	133.8	133.2	133.4	132.9
C_{8a}	130.8	130.9	131.5	130.5	131.0	130.5	132.7	136.2 ^c
C_α	201.9	193.6	168.1	183.1	215.2	199.5	230.5	197.8
CH_3	30.6				26.3		31.5, 35.6	22.9
(b) 2-Naphthyl System								
C_1	130.6	134.6		138.2	146.3	154.8	153.2	167.5
C_2	134.9	134.9		116.0	126.3	126.1	137.8	140.2
C_3	124.2	123.1		123.4	123.1	122.2	128.4	127.5
C_4	128.9	129.6		130.4	130.8	131.9	132.1	133.5
C_5	128.2	128.5		128.7	128.7	129.2	129.8	130.6
C_6	128.9	129.6		133.3	135.9	137.4	142.8	146.4
C_7	127.1	127.5		128.2	129.3	129.6	130.8	131.4
C_8	130.1	130.1		130.9	132.6	133.3	137.8	139.5
C_{4a}	136.0	136.7		138.5	140.7	141.7	145.5	147.4
C_{8a}	133.0	133.0		131.3	132.1	132.2	133.2	133.8
C_α	197.9	192.4		181.5	216.0	200.7	241.8	216.1
CH_3	27.2				23.8		31.8, 31.2	25.2

^a Chemical shifts for naphthalene are: $\text{C}_{1,4,5,8} = 127.7$, $\text{C}_{2,3,6,7} = 125.6$, $\text{C}_{4a,8a} = 133.3$, from R. S. Ozubko and G. W. Buchanan, *Can. J. Chem.*, **52**, 2493 (1974). ^b Resonance could not be detected. ^c Interchangeable values.

Table IV. Least-Squares Analysis of Chemical Shift Response Patterns in Arylcarbenium Ions

Position	Slope	Intercept	SD ^a	cc ^b	n ^c
(a) Phenyl System					
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) Phenylethynyl System					
β	1.287	-91.0	9.39	0.768	10
γ	4.159	-464.8	9.13	0.970	10
1	-0.053	125.2	1.79	-0.251	10
2,6	0.350	86.8	0.35	0.993	10
3,5	0.086	117.8	0.32	0.922	10
4	0.558	57.5	0.62	0.992	10
(c) 1-Naphthyl System					
1	0.214	98.9	8.74	0.277	7
2	0.681	44.4	5.61	0.814	8
3	0.112	110.0	0.51	0.929	8
4	1.052	-5.8	0.94	0.997	8
5	0.152	108.9	0.29	0.986	8
6	0.081	116.8	0.47	0.893	8
7	0.301	89.3	0.75	0.977	8
8	-0.089	138.0	1.35	-0.607	8
4a	-0.054	141.6	0.25	-0.927	8
8a	0.135	112.3	1.39	0.744	8
(d) 2-Naphthyl System					
1	1.172	-24.3	3.72	0.965	7
2	0.244	95.3	8.84	0.308	7
3	0.153	102.3	1.93	0.682	7
4	0.144	110.0	0.28	0.987	7
5	0.075	118.2	0.26	0.958	7
6	0.605	48.2	0.57	0.997	7
7	0.150	107.2	0.20	0.994	7
8	0.339	84.1	1.10	0.964	7
4a	0.399	82.8	0.52	0.994	7
8a	0.029	128.5	0.85	0.366	7

^a Standard deviation. ^b Correlation coefficient. ^c Number of chemical shifts included in the analysis.

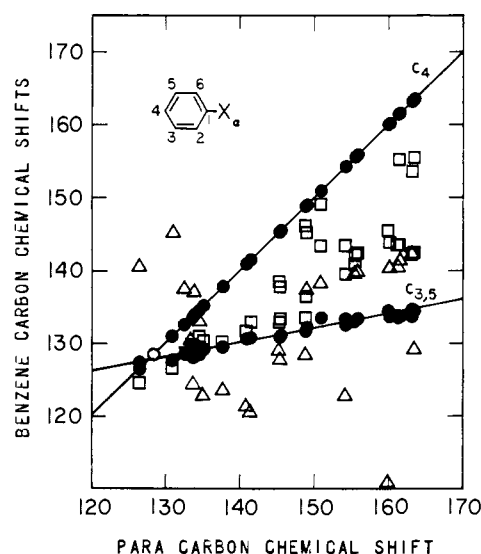


Figure 1. Carbon chemical shift response patterns for the phenyl system. Open squares represent shifts of ortho carbons, $\text{C}_{2,6}$, and triangles represent the ipso carbons, C_1 .

from the γ -substituent effect (see discussion in ref 9). "Special" influences of the nearby substituents also appear to be operative at the directly substituted ipso position, as evidenced by the lack of any regularity in the chemical shift response pattern. Factors other than π electronic effects are labeled "special" influences here for the sake of convenience. "Special" influences at the site of substitution or adjacent ortho positions may include σ inductive effects, substituent magnetic anisotropies, steric interactions, diamagnetic shielding by neighboring groups, and perhaps other unidentified neighboring group effects.¹⁰ The scattered points in the plots of $\delta_{\text{C}} \text{C}_{2,6}\text{-Ph}$ and $\delta_{\text{C}} \text{C}_1\text{-Ph}$ vs. the reference $\delta_{\text{C}} \text{C}_4\text{-Ph}$ are representative of the general case: linear

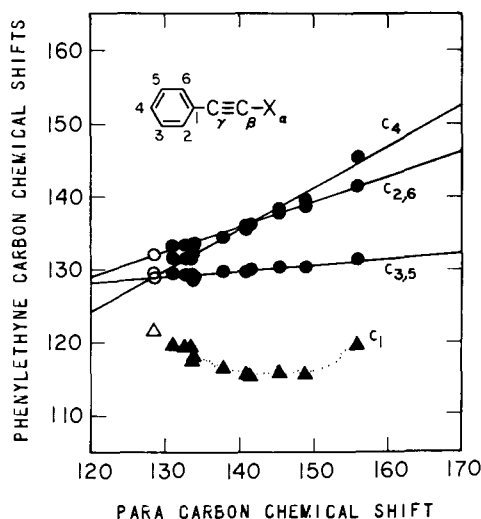


Figure 2. Carbon chemical shift response patterns for the phenylethyne system.

chemical shift response patterns are found only for aryl carbons in positions more remote from the site of substitution than the directly substituted position and immediately adjacent, ortho-type positions.

The Phenylethyne System. In the phenylcarbenium ion series discussed above, the ortho and ipso positions have scattered chemical shift response patterns due to "special" influences of the nearby substituents. The interposition of a triple bond between the phenyl ring and the substituents should reduce or eliminate the scatter if the through-bond or through-space distance to the substituent is important. This postulate is confirmed by Figure 2 which shows the response patterns of the phenyl carbons in the phenylethyne-carbenium (PhE) system. The ortho-type position now gives a good linear correlation in the plot of δ_C C_{2,6}-PhE vs. δ_C C₄-Ph, with $m = 0.350$. The meta and para positions also exhibit linear response patterns, with $m = 0.086$ and 0.558 , respectively.

The response pattern of C₁ is a curve as shown in Figure 2, but the pattern is obviously more regular than the pattern for the ipso position in the phenyl system. As the strength of the electron withdrawing groups increase, C₁ initially becomes more shielded, but then the pattern levels out, and finally turns toward less shielding in the phenylethyndimethylcarbenium ion. Probably the initial shielding response is the result of polarization of the phenyl electron distribution, with a resultant gain in electron density at C₁; theoretical studies have shown that such polarization is important in phenyl derivatives.²⁷ The upward turn in the response pattern indicates that the polarization effect may be counterbalanced by electron withdrawal in the presence of very strong electron withdrawing groups.

The directly substituted ethynyl position, C_β, gives an irregular chemical shift response pattern. The C_β shifts also do not correlate well with δ_C C₁-Ph ($m = 1.42$, $cc = 0.701$), although the ipso positions in the 1- and 2-naphthyl systems and some heteroaryl systems²⁸ do correlate well with the δ_C C₁-Ph. The other ethynyl position, C_γ, is conjugated with the carbenium center in simple resonance theory, and gives a strongly positive response pattern, as expected. However, the C_γ pattern is not linear; a plot of δ_C C_γ-PhE vs. δ_C C₄-Ph shows a pronounced upward curvature.

The 1-Naphthyl System. The carbon chemical shift response patterns for the 1-N system are shown in Figure 3, in which the δ_C C-1-N are plotted vs. the reference δ_C C₄-Ph from the analogously substituted benzenes. The re-

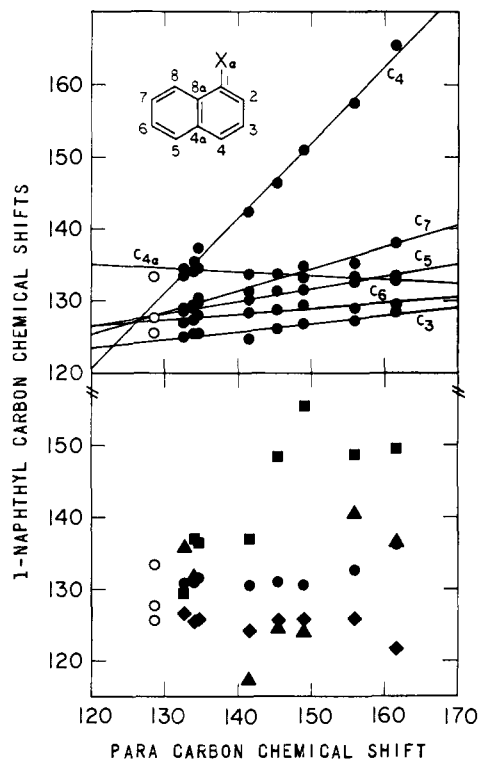


Figure 3. Carbon chemical shift response patterns for the 1-naphthyl system. Upper plot shows response patterns of positions remote from the site of substitution. Lower plot shows response patterns of peri-, ortho- and ipso-type carbons: $\blacktriangle = C_1$, $\blacksquare = C_2$, $\blacklozenge = C_8$, and $\bullet = C_{8a}$.

gression analysis of the response patterns is presented in Table IV.

The 1-N system has six ring positions which may be considered as being remote from the site of substitution: C₃, C₄, C_{4a}, C₅, C₆, and C₇. The δ_C for all six positions give linear correlations when plotted vs. δ_C C₄-Ph, with $SD < 1.00$ as indicated in Table IV. Simple resonance structures for **3** indicate that charge is delocalized to positions C₄, C₅, and C₇ (also C₂ and C₈ which are not remote from the site of substitution). These conjugated positions have steeper positive response slopes than those corresponding to positions C₃, C_{4a}, and C₆, which are uncharged in resonance theory. The steepest slope is found for C₄-1-N, which is analogous to the para position in the phenyl system.

The directly substituted position, C₁, shows the expected scatter in its response pattern. However, the δ_C C₁-1-N do correlate fairly well with the δ_C C₁-Ph ($m = 1.05$, $cc = 0.969$), which indicates that the same substituent influences which produce scatter in the C₁-Ph response pattern are also operative in the 1-N system. The ortho-type positions, C₂-1-N and C_{8a}-1-N, give chemical shift response correlations with $SD > 1.00$. The remaining position, C₈-1-N, is not an ipso or ortho-type position, but it also has a $SD > 1.00$ for the correlation with δ_C C₄-Ph. C₈-1-N is in a peri position in relation to the C₁ substituents, which presumably places it close enough to be affected by the same types of "special" substituent influences felt at ortho carbons.

The 2-Naphthyl System. Carbon chemical shift response patterns for the 2-N system are shown in Figure 4, and the linear regression results are found in Table IV.

The 2-N system has seven ring positions which are more remote from the site of substitution than the ipso position and ortho-type positions (C₁ and C₃). Five of the positions (C₄, C₅, C₆, C₇, and C_{4a}) give linear response patterns, but two of the positions (C₈ and C_{8a}) give curved response patterns. The curved response pattern for C_{8a}-2-N is similar to

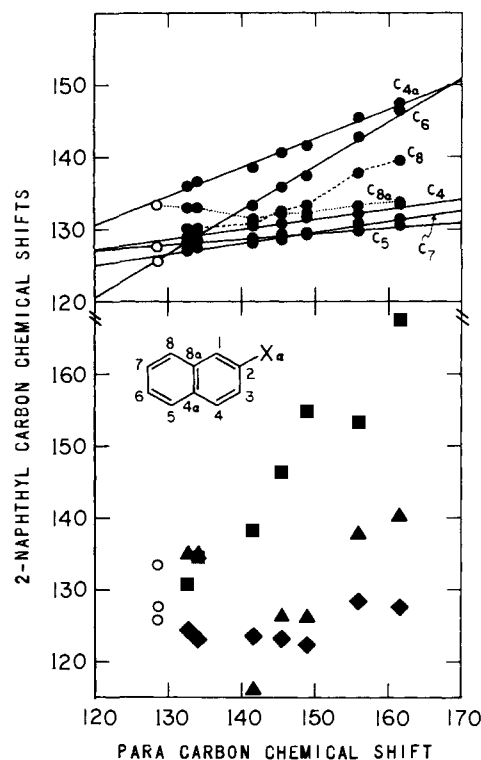


Figure 4. Carbon chemical shift response patterns for the 2-naphthyl system. Upper plot shows response patterns of positions remote from the site of substitution. Lower plot shows response patterns of ortho- and ipso-type carbons: \blacksquare = C_1 , \blacktriangle = C_2 , and \blacklozenge = C_3 .

the curved pattern observed for C_1 -PhE and may analogously be due to polarization of the electron density in the benzo portion of the 2-N system toward C_{8a} , as the electron withdrawing capability of the substituents increase. However, the overall response of C_{8a} -2-N, as indicated by the slope of the correlation line (Table IV), is quite small, in agreement with simple resonance theory which predicts no charge at C_{8a} in 4. Similarly, the other position which gives a curved response, C_3 -2-N, shows a definite trend toward a positive response slope, in agreement with simple resonance theory which predicts charge development at C_8 -2-N. Among the five positions which give good linear response patterns, positions C_{4a} -2-N and C_6 -2-N have steeper positive slopes than positions C_4 -2-N, C_5 -2-N, and C_7 -2-N, also in agreement with the predictions of resonance theory.

The directly substituted ring carbon, C_2 -2-N, gives a very scattered chemical shift response pattern, but the δ_C C_2 -2-N correlate excellently with δ_C C_1 -Ph ($m = 1.108$, $cc = 0.998$). As in the case of C_1 -1-N, this excellent correlation indicates the similarity of substituent influences on the chemical shifts at the directly substituted position in the phenyl and naphthyl ring systems. The chemical shift response patterns of the ortho-type positions, C_1 -2-N and C_3 -2-N, exhibit the usual scatter. Despite the scatter, a strong positive response is evident in the δ_C C_1 -2-N vs. δ_C C_4 -Ph plot, which suggests considerable charge development at C_1 -2-N.

Comparison with Calculated Charge Densities

The linear response patterns of carbon chemical shifts described in the preceding section are empirical evidence of a systematic dependence of arene carbon chemical shifts on the electronic effects of substituents. It has previously been demonstrated that the δ_C at C_4 in monosubstituted benzenes reflect the charge densities at the para position. Therefore, it is reasonable to anticipate a similar relation-

Table V. Calculated Changes in Charge Density for $Ar \rightarrow ArCH_2^+$

Position	HMO	SCF- π	CNDO/2 total	CNDO/2 π	CNDO/2 regional
(a) Phenyl System					
C_α	0.571	0.436	0.231	0.502	0.405
C_1	0.000	-0.013	-0.004	-0.050	0.001
$C_{2,6}$	0.143	0.147	0.109	0.178	0.158
$C_{3,5}$	0.000	0.042	-0.022	-0.025	0.039
C_4	0.143	0.200	0.140	0.242	0.199
(b) Phenylethynyl System					
C_α	0.364	0.484	0.253	0.493	0.463
C_β	0.000	-0.009	0.061	-0.079	-0.001
C_γ	0.364	0.259	0.219	0.374	0.219
C_1	0.000	-0.033	-0.047	-0.091	-0.047
$C_{2,6}$	0.091	0.064	0.065	0.098	0.091
$C_{3,5}$	0.000	0.031	-0.008	-0.013	0.033
C_4	0.091	0.109	0.078	0.133	0.118
(c) 1-Naphthyl System					
C_α	0.450	0.326	0.160	0.378	0.306
C_1	0.000	-0.010	0.004	-0.035	0.009
C_2	0.200	0.184	0.142	0.242	0.190
C_3	0.000	0.019	-0.048	-0.065	0.011
C_4	0.200	0.225	0.170	0.298	0.221
C_5	0.050	0.084	0.061	0.093	0.094
C_6	0.000	0.043	-0.003	-0.001	0.041
C_7	0.050	0.107	0.072	0.115	0.112
C_8	0.000	0.010	-0.018	-0.032	0.001
C_{4a}	0.000	-0.017	-0.037	-0.059	-0.037
C_{8a}	0.050	0.030	0.051	0.064	0.051
(d) 2-Naphthyl System					
C_α	0.529	0.381	0.194	0.437	0.348
C_1	0.235	0.210	0.158	0.279	0.199
C_2	0.000	-0.009	0.002	-0.042	0.009
C_3	0.059	0.050	0.035	0.048	0.075
C_4	0.000	0.048	0.001	0.010	0.047
C_5	0.000	0.026	-0.016	-0.024	0.021
C_6	0.059	0.116	0.081	0.139	0.123
C_7	0.000	0.045	-0.002	-0.002	0.041
C_8	0.059	0.067	0.061	0.093	0.091
C_{4a}	0.059	0.074	0.075	0.112	0.075
C_{8a}	0.000	-0.007	-0.032	-0.050	-0.032

ship at arene ring positions which show a similar response to substituent effects, as demonstrated by their chemical shift response patterns. Qualitatively, the relationship of chemical shifts to charge is apparent in the observed tendency for positions conjugated with the carbenium center to have steeper chemical shift response slopes than nonconjugated positions.

In order to put these observations on a more quantitative level, we compare the chemical shift response patterns with molecular orbital calculations of charge densities. In the experiments, the changes in chemical shifts are observed in a progression from uncharged systems toward the parent arylcarbenium ion, so the observed response slopes at each position i are compared with changes in charge density (Δq_i) at the corresponding positions, calculated for the process of the neutral arene being converted to the arylcarbenium ion:



The calculated changes in charge density between the arene and arylcarbenium ion are listed in Table V for all of the positions in the Ph, PhE, 1-N, and 2-N systems. Calculations of charge densities were performed using three different MO methods: the simple HMO method,²⁹ a PPP SCF- π method,³⁰ and the all-valence-electron CNDO/2 method.³¹ The HMO and SCF- π methods yield only π charge densities, but from the CNDO/2 method, the π charge densities, total carbon charge densities ($\pi + \sigma$), and regional charge densities are listed. The regional charge

Table VI. Least-Squares Analysis of Chemical Shift Response Slopes^a vs. Changes in Charge Density (Δq_i)^b

MO method	Slope	Intercept	SD ^c	cc ^d	n ^e
(a) All positions with SD < 1.00 ^a					
HMO	5.14	0.08	0.12	0.939	17
SCF- π	4.77	-0.03	0.09	0.960	17
CNDO/2 total	4.68	0.15	0.13	0.924	17
CNDO/2 π	2.89	0.14	0.11	0.946	17
CNDO/2 regional	4.33	0.00	0.11	0.940	17
(b) Excluding C _{5,6,7} -1-N					
HMO	5.13	0.10	0.12	0.947	14
SCF- π	4.87	0.00	0.05	0.990	14
CNDO/2 total	4.87	0.18	0.10	0.963	14
CNDO/2 π	2.97	0.17	0.08	0.977	14
CNDO/2 regional	4.48	0.03	0.08	0.978	14

^a Slopes from Table IV. ^b From Table V. ^c Standard deviation. ^d Correlation coefficient. ^e Number of points.

density is defined as the sum of the charges on a carbon atom and any hydrogen atoms bonded to it. The concept of regional charge was introduced by Streitwieser, who noted the similarity between CNDO/2 regional charges and PPP SCF- π charges.^{32,33} The use of regional charges may correct for a problem of population analysis in the partitioning of charge between carbon and hydrogen, which is highly dependent upon the relative choice of parameters for carbon and hydrogen in CNDO/2 calculations.^{32,33}

Standard geometries³⁴ were used in the calculations because the geometries of the cations are not known. At this level of approximation, we felt it unnecessary and perhaps unwise to make arbitrary adjustments in the molecular geometries. With the exception of the phenylethynyl system, all C-C bonds were 1.40 Å, C-H bonds were 1.08 Å, and bond angles were 120°. In the phenylethynyl calculations, the triple bond was 1.20 Å, the ring-C(sp) bond was 1.45 Å, the C(sp)-H bond was 1.06 Å, and the C(sp)-CH₂⁺ bond was 1.40 Å.

In Table VI, the response slopes for the 17 positions in the Ph, PhE, 1-N, and 2-N systems which gave linear response patterns with SD < 1.00 (Table IV) are compared with the charge calculations of Table V. The best correlation was obtained with SCF- π charges. The correlations with HMO charges, CNDO/2 π charges, and CNDO/2 regional charges are of comparable quality, while the correlation with the total carbon charges calculated in the CNDO/2 method is actually the poorest.

Examination of the plot of chemical shift response slopes vs. calculated changes in SCF- π charge density, Figure 5, shows that the three most deviant points are for positions in the benzo portion of the 1-N system, the C₅-1-N, C₆-1-N, and C₇-1-N positions. If these points are disregarded, the correlation with SCF- π charges improves markedly, as indicated in Table VI. The elimination of these points also significantly improves the correlations with CNDO/2 charges, while the correlation with HMO charges improves only slightly. The SCF MO calculations may overestimate the amount of charge delocalized into the benzo portion of the 1-N ring system, perhaps because standard geometries were used and no attempt was made to correct for the differences in bond lengths expected to exist between the arene and the arylcarbenium ion. However, Figure 5 does illustrate that the overall correspondence between chemical shift response patterns and calculated changes in charge densities is quite good.

The intercepts of the regression lines listed in Table VI are also interesting. In a correlation of chemical shifts with

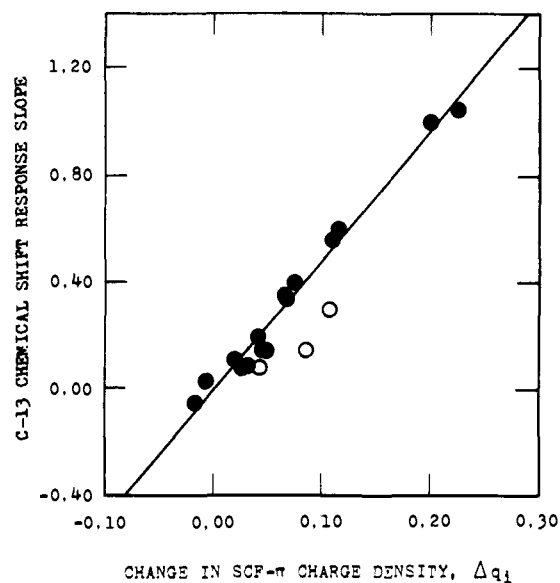


Figure 5. Plot of carbon chemical shift response slopes vs. calculated changes in SCF- π charge density. The C_{5,6,7}-1-N positions are marked by open circles and were not used to determine the correlation line in the figure.

charge, it is reasonable to expect that zero charge development at an arene ring position should result in no changes in the chemical shift, and therefore the correlation line should pass through the origin. By this criterion, the correlation with SCF- π charges is still the best, with an intercept of nearly zero. CNDO/2 regional charges are also good in this respect, but the correlations with HMO, CNDO/2 total, and CNDO/2 π charges are poor. In the HMO method, positions not formally conjugated with the carbenium center are calculated to have zero charge development despite having positive chemical shift response patterns. In the CNDO/2 method, there is a tendency toward charge alternation in the π and total charges, such that the formally nonconjugated positions become negatively charged. To the extent that carbon chemical shifts can be considered as a measure of charge densities, our experimental results support the picture of charge distribution obtained in the SCF- π and CNDO/2 regional charge calculations, in which some positive charge is delocalized to most of the positions in arylcarbenium ions, including even the formally nonconjugated positions. It could be argued that positive carbon chemical shift response slopes at the nonconjugated positions are found not because of charge development at those positions but because of some deshielding resulting from charge development at adjacent positions; similar arguments have been suggested for proton chemical shifts.³⁵ However, the negative response slope found for C_{4a}-1-N (Table IV) suggests that deshielding relayed from adjacent charged positions is probably not significant.

We report this rather simplistic correlation with charge densities, in which we neglect bond orders and excitation energies,¹³ because of the remarkable success of the simple correlation, and not because we believe it to be the most theoretically sophisticated approach^{4,15} to predicting or interpreting carbon shifts. These results are part of an investigation designed to discover what ¹³C NMR data really mean in regard to structure and charge distribution in carbocations. It is apparent from the present results that a simple relationship between carbon shifts and charge in arylcarbenium ions occurs only at positions sterically remote from the carbenium center, but at these remote positions the correspondence with charge densities is quite good.

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 External (capillary) $\text{Si}(\text{CH}_3)_4$ was used as the chemical shift reference. Although different types of solvents were used for the neutral members (CDCl_3 and CCl_4) and cationic members (SO_2 and SO_2ClF) of each series, corrections of chemical shifts for differences in bulk susceptibility do not have to be made because Figures 1–4 compare chemical shifts to a reference series of shifts ($\delta_{\text{C}} \text{C}_4\text{-Ph}$) determined in the same type of solvent for each kind of substituent. In other words, the quantities discussed in the text are relative quantities, not absolute chemical shifts. The spectra of the carbocations were measured in a range from -40 to -80 °C; no significant temperature dependence of the chemical shifts was observed in this range. Spectra of the neutral species were measured at the ambient operating temperature unless otherwise noted. Details of sample preparation are given below.

Most of the phenylcarbenium ion derivatives have been prepared previously and their ^{13}C NMR spectra recorded, as noted in Table I. High purity commercial samples of α -methylstyrene and benzoyl fluoride were used as $\sim 25\%$ solutions in CCl_4 , and benzamide was used as a saturated solution in CDCl_3 . $\text{Ph-C}(\text{OH})\text{NH}_2^+$ was obtained by the addition of benzamide to FSO_3H in SO_2 at -78 °C (dry ice–acetone bath temperature). $\text{Ph-CHCH}_2\text{CH}_3^+$ was prepared by addition of 1-phenyl-2-chloropropane in SO_2ClF at -78 °C to a 1:1 v/v solution of HF-SbF_5 (1:1) in SO_2ClF at -78 °C, followed by warming to -40 °C to complete the ionization and rearrangement; $\text{Ph-C}(\text{CH}_3)\text{CH}_2\text{CH}_3^+$ was similarly prepared using commercially available neophyl chloride as the precursor.³⁷ 1-Phenyl-2-chloropropane was synthesized by chlorination of 1-phenyl-2-propanol with thionyl chloride at -60 °C.³⁸

In the PhE series, high purity commercial samples of 4-phenylbut-2-yn-2-one (in SO_2 at -40 °C), phenylpropynoic acid (in acetone- d_6 at -60 °C), ethyl phenylpropynoate (in SO_2ClF at -40 °C), and phenylpropynal (in SO_2 at -60 °C) were used. The spectrum of phenylpropynoyl fluoride was described previously.³⁹ Phenylpropynamide (in SO_2 at -40 °C) was synthesized from ethyl phenylpropynoate by the procedure of Iwai and Nakamura.⁴⁰ $\text{PhE-C}(\text{OH})\text{NH}_2^+$, $\text{PhE-C}(\text{OH})_2^+$, $\text{PhE-C}(\text{OH})\text{OCH}_2\text{CH}_3^+$, $\text{PhE-C}(\text{OH})\text{CH}_3^+$, and PhE-CHOH^+ were prepared by protonation of the corresponding carbonyl precursors by addition of a solution of the precursor in SO_2 to a 1:1 v/v solution of FSO_3H in SO_2 at -78 °C. The preparation of $\text{PhE-C}(\text{CH}_3)_2^+$ has been described previously.³⁹

In the 1-N series, 1'-acetonaphthone, 1-naphthaldehyde, and 1-naphthyl chloride were commercial samples used as $\sim 25\%$ solutions in CDCl_3 . $1\text{-N-C}(\text{OH})_2^+$ was prepared by the addition of powdered 1-naphthoic acid (commercially available) to a 1:2 v/v solution of FSO_3H in SO_2ClF at -78 °C. $1\text{-N-C}(\text{OH})\text{CH}_3^+$ and 1-N-CHOH^+ were similarly prepared by addition of solutions of the ketone and aldehyde precursors in SO_2ClF to $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ solutions at -78 °C. $1\text{-N-C}(\text{CH}_3)_2^+$ and 1-N-CHCH_3^+ were prepared by ionization of 2-(1-naphthyl)propan-2-ol and 1-(1-naphthyl)ethyl alcohol in 1:1 $\text{FSO}_3\text{H-SbF}_5$ in SO_2ClF solution at -78 °C, by the addition of SO_2ClF solutions of the alcohols at -78 °C to the acid medium. The alcohols were synthesized by the reaction of methylmagnesium iodide with 1'-acetonaphthone and 1-naphthaldehyde.⁴¹

In the 2-N series, 2'-acetonaphthone and 2-naphthaldehyde were commercial samples used as $\sim 25\%$ solutions in CDCl_3 . $2\text{-N-C}(\text{OH})_2^+$, $2\text{-N-C}(\text{OH})\text{CH}_3^+$, and 2-N-CHOH^+ were obtained by protonation of the corresponding carbonyl precursors by the addition of the precursor to a 1:1 v/v solution of FSO_3H in SO_2ClF at -78 °C. The sample of 2-naphthoic acid used for the protonation study was synthesized by the mixing of an ether solution of 2-iodonaphthalene with 2.1 N *n*-butyllithium in hexane (Alfa Inorganics) at -78 °C, followed by quenching of the mixture with dry ice and workup with aqueous HCl. $2\text{-N-C}(\text{CH}_3)_2^+$ and 2-N-CHCH_3^+ were prepared by ionization of 2-(2-naphthyl)propan-2-ol and 1-(2-naphthyl)ethyl alcohol. The ionizations were carried out by the slow addition of SO_2ClF solutions of the alcohols to vigorously stirred solutions of 1:1 $\text{FSO}_3\text{H-SbF}_5$ in SO_2ClF at -78 °C. 2-(2-Naphthyl)propan-2-ol was synthesized from 2'-acetonaphthone through the use of methylmagnesium iodide, and 1-(2-naphthyl)ethyl alcohol was synthesized by reduction of the ketone with NaBH_4 .

phthone through the use of methylmagnesium iodide, and 1-(2-naphthyl)ethyl alcohol was synthesized by reduction of the ketone with NaBH_4 .

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Supplementary Material Available: Detailed discussion of peak assignments in the naphthyl systems (7 pages). Ordering information is given on any current masthead page.

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